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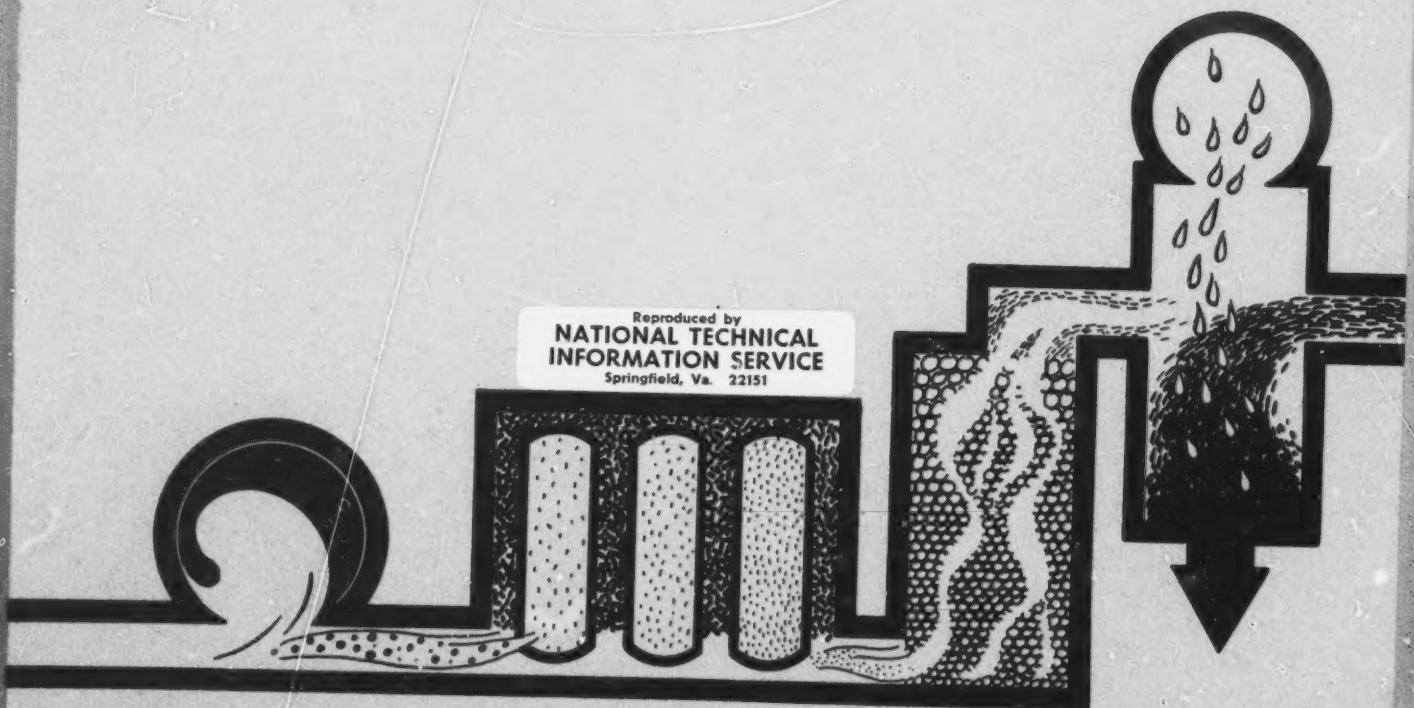


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Effect of Porous Structure on Carbon Activation

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16. Abstract Two carbon samples, one a calcined Elkol, Wyoming coal and the other a graphite, were reacted with gases in a carbon activation system. Reaction rates and porous structures of the coal, after activation by air and by carbon dioxide, and the graphite, after activation by carbon dioxide, were measured. Total, macropore, and micropore volumes, surface area, and pore-size distributions were measured as functions of burnoff. In 1 mm diameter calcined coal particles, the overall reaction rate was chemical rate limited at temperatures up to 961°C and rates as high as 106%/hour. In 19 mm diameter graphite cylinders, the rate at 1030°C was diffusion limited. Pore volume changes in calcined coal occurred due to heating, carbon burnoff, and opening of closed pores, whereas pore volume changes in graphite were produced mainly by end-burning of crystal-lites. Up to 12% burnoff, closed pores that were opened were micropores; above 12% burnoff they were macropores. Although pore growth can be described, cannot yet be quantitatively predicted. However, these results have suggested that activation of carbons containing crystallites of a given size range could be a means of producing an activated carbon with pores of that size range, and further studies are recommended.

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Abstractor Mark V. Lowry

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EFFECT OF POROUS STRUCTURE
ON CARBON ACTIVATION

by

University of Colorado
Chemical Engineering Department
Boulder, Colorado

for the

ENVIRONMENTAL PROTECTION AGENCY

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June 1971

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ABSTRACT

Reaction rates and porous structures of a calcined Wyoming coal activated by air and by carbon dioxide and a graphite activated by carbon dioxide were measured. Total, macropore and micropore volumes, surface area and pore-size distributions were determined as functions of burnoff.

In 1-mm-diameter calcined coal particles, the overall reaction rate was chemical rate limited at temperatures as high as 961° C and rates as high as 106%/hr. In 19-mm-diameter graphite cylinders, the rate at 1030° C was diffusion limited. In graphite, pore growth by end-burning of crystal-lites was an important mechanism. In calcined coal, pore-volume changes occurred due to heating, carbon burnoff and the opening of closed pores present in the starting material. Burnoff of carbon occurred essentially entirely in macropores. Up to 12% burnoff, the closed pores that were opened were micropores; above 12% burnoff they were macropores.

In order to develop large micropore volumes and hence large surface areas by gas activation, a micropore structure must be present in the starting material.

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SECTION I

CONCLUSIONS

1. In the activation of 1-mm-diameter particles of a Wyoming coal with carbon dioxide, the rate of reaction was chemical reaction controlled up to reaction rates of 106%/hr and temperatures as high as 961°C.
2. The pore structure of the calcined coal was affected by heating in nitrogen or helium at temperatures as low as 880°C. The effect of heating was generally to cause total pore volume and macropore (pores greater than 100 Å radius) volume to increase and micropore (pores less than 100 Å radius) volume to decrease.
3. In the activation of purified graphite cylinders (19 mm in diameter) in carbon dioxide at 1030°C, the overall reaction rate was diffusion limited. Pore growth in graphite occurred by end-burning of graphite crystallites and by wall-burning of pores. The former predominated as long as crystallites were available.
4. Gas activation of the calcined coal resulted in increases in the pore volume and surface area by removal of carbon and by making accessible closed pores present in the starting material.
5. Essentially all removal of carbon by burning occurred in macropores.
6. At burnoffs up to 12% in air and up to 400°C, the closed pores that were opened by activation contributed to the micropore volume. At burnoffs of 15% and greater in carbon dioxide, and at 800°C and above, the closed pores that were opened contributed to the macropore volume.
7. The surface of porous carbons was not uniformly reactive to oxidizing gases. This was probably due to a non-uniform distribution of reactive sites.
8. In order to develop large micropore volumes and hence large surface areas in the gas-activation of coal, it is necessary that the starting material contain a substantial network of micropores since few new micropores are formed by burning.

SECTION II

RECOMMENDATIONS

Pore growth in gas-activated carbons can be described but not yet quantitatively predicted. The surface of carbons appears to be non-uniformly reactive to oxidizing gases. Further progress in understanding and predicting pore growth will require investigation of the nature and distribution of reactive sites on the surface.

Pore growth is influenced by preheating the carbon, by the activating gas composition, and by the temperature of activation. Preheating tends to decrease micropore volume. It is recommended that in activation and re-activation of carbons, preheating in non-reactive gases be minimized. Micropore-volume increases occur mainly at low burnoffs. It is therefore recommended that the maximum burnoff in activation should probably be about 15 to 20%.

In the activation of graphite, the end-burning of graphite crystallites to produce pores of sizes comparable to the crystallites is an important mechanism. This suggests that activation of carbon structures containing crystallites of a given size range could be a means of producing an activated carbon with pores of that size range. It is recommended that studies to determine the feasibility of such a procedure be conducted.

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SECTION III

INTRODUCTION

Recognizing the potential value of activated carbons for removal of water pollutants, the present study was initiated for the general purpose of obtaining information on the effect of the porous structure of carbon on carbon activation. It was the basic postulate of this investigation that the initial porous structure of a carbon exerts a profound influence on the course of the activation reaction and consequently on the pore structure of the activated carbon product. The term "porous structure" is used here to mean the surface area, pore volume, and the distribution of pore volume and surface area with respect to pore size.

The aims of this work were: 1) to study the effects of porous structure of the starting material on the rate of carbon reaction, and 2) to study the relationships between the porous structure of the starting material and the porous structure of the resulting activated carbon. The basic raw material was a calcinate produced from an Elkol coal from Wyoming. The principal variables were reaction temperature, gas composition and porous structure of the carbon. The results for porous structure and reaction rates were interpreted on the basis of additional studies, done as part of this work, on reaction kinetics and diffusion. It was anticipated that the information resulting from this work could be useful in commercial activation processes to suggest means of producing carbons with "tailored" porous structures and means of reducing the costs of producing activated carbon.

Adsorbent carbons have a major role in wastewater treatment processes to meet improved water quality standards. Carbon adsorption as a tertiary treatment process to remove refractory organic substances from domestic sewage and industrial waters has been demonstrated in several cases (1, 2, 3). Recent process developments have shown the applicability of carbon adsorption, combined with coagulation-filtration, as a potential replacement for traditional secondary (biological) treatment, as well as accomplishing refractory organic removal (4).

The widespread use of activated carbons in water pollutant removal is limited by its expense (1, 5). Activated carbons are relatively expensive, ranging in cost from about \$0.07 to over \$0.70 per lb (6). The cost of carbon-adsorption wastewater-treatment processes usually is strongly influenced by the initial and replacement cost of carbon (1, 2). The quantity, and thus cost, of carbon is dependent upon its capacity (i.e., the amount of pollutant adsorbed per unit mass of carbon) which in turn determines the frequency with which the carbon must be regenerated, and upon the amount of adsorptive capacity lost during regeneration.

Activated carbon is a class of carbonaceous materials with the property of adsorbing various chemical compounds from either the gaseous or liquid state. Activated carbons can be made from virtually any carbon-containing substance and have been made from many substances of living origin, ranging from wood to blood and from petroleum coke to coconut shells (7). The most notable common characteristic of activated carbons is a very high internal surface area per unit mass, ranging from perhaps 100 to 2,000 m²/g, but generally in the neighborhood of 1,000 m²/g. In order to obtain such high areas, it is necessary that the carbon be pierced by a network of very fine openings or pores.

The preparation of an activated carbon from a carbon source generally involves three main steps: grinding or compacting to give a desired particle size, carbonization and activation. Carbonization is the heating of the raw material in an inert atmosphere to drive off volatile substances and increase the proportion of carbon. Changes in both the porous structure and chemical properties of the material occur during carbonization. Activation is the reaction of the carbonized char with some reactant, usually an oxidizing gas (steam, carbon dioxide or oxygen), to remove portions of the material leaving voids (pores) behind and to create active functional groups on the surface. The technology of activation is largely proprietary within the industry (7).

The properties of an activated carbon are determined by the raw material from which it is made and the process by which it is made. The raw materials are generally relatively inexpensive; e.g., coals which typically cost of-the-order of \$5 per ton. The cost of activated carbon is then due mainly to the processing required to convert the raw material to activated form.

Coal is an attractive raw material for activated carbon production, due to its low cost and great abundance. Some work has been done on coal itself as an adsorbent for wastewater treatment (8), but the use of coal does not seem to be attractive (9). Some commercial activated carbons are prepared from coal (6).

The properties of activated carbon that are of immediate importance in determining its usefulness include: cost, physical strength, adsorptive capacity and particle size. The adsorptive capacity is related to the surface area per unit mass and the interaction of the surface with specific adsorbates; it is determined by the inherent properties of the carbon and by the degree of activation. Descriptive properties of carbons most often measured are: surface area and the adsorptive capacity for particular adsorbents. For liquid-phase adsorbent carbons, iodine number, molasses number, methylene blue number and alkyl benzene sulfonate (ABS) number are frequently reported. For any particular application it is necessary to test various carbons

to find an appropriate one because, while the usual tests are useful indicators, none can completely predict the performance of a carbon for any adsorbate (6).

The amount of surface area per unit mass of carbon, the accessibility of that surface to adsorbate molecules and the concentration on the surface of sites capable of attracting and holding specific adsorbates are the keys to the adsorptive capacity of a carbon. Surface areas are routinely measured, usually by the classical Brunauer-Emmett-Teller (BET) method, from gas adsorption data (10). The accessibility of surface and the interaction of the surface with a particular adsorbate are difficult to determine. Recent studies have been successful in directly identifying certain functional groups on carbon surfaces (11), and this type of information promises to enhance the understanding of carbon adsorption.

There have been several studies of the influence of porous structure on the adsorptive properties of carbon and other adsorbents. Most of the work has been for physical adsorption of gases (12); indeed, gas adsorption is one of the principle tools for the analysis of porous structure. The equilibrium amount of gas physically adsorbed on a solid surface is directly related to the amount of surface area accessible to the gas molecules. The amounts of certain solutes adsorbed from aqueous solution have been correlated with the cumulative surface area of pores greater than specific sizes; e.g., iodine number has been reported to correlate with area of pores greater than 10Å diameter, and molasses number with area of pores greater than 28Å diameter (13). In other cases, a correlation between the amount of a specific solute adsorbed and surface area has not been obtained; e.g., acetic acid and hydrogen ion (14,17). The lack of correlation may be due to incomplete knowledge of the porous structure of the adsorbent or due to a specific interaction between the solute and functional groups on the carbon surface. It would seem possible that functional groups are not uniformly distributed on the surface.

The situation can be expected to be even more difficult when a mixture of solutes (and possibly colloidal particles) is present, such as in domestic sewage or many industrial wastes. Not only may a variety of molecular and particle sizes be present, but species may compete for adsorption sites, and there may be only a gross measure of species concentrations such as COD, BOD or TOC. In view of this, it is not surprising that the adsorptive capacity for sewage constituents does not correlate well with surface area (6).

Clearly, the tailor-making of adsorbents for various adsorbates would require detailed knowledge of the influence of the porous structure of the adsorbent, the molecular size of the adsorbate and the mechanism of adsorption.

The rate of uptake of adsorbates is also a distinct function of the porous structure of the adsorbent and the character of the adsorbate. This is well established both theoretically and experimentally for gases (15). For liquids, the theoretical basis is not as well established as for gases, but ordinary diffusion theory applied to porous solids must take into account the available diffusion path (and hence the porous structure) even for liquids (16).

Since there is no standard nomenclature for designating ranges of pore sizes, herein the following definitions will be used: macropores are pores with radii greater than 0.01μ ($1\mu = 10^{-6}\text{ m} = 10^4 \text{ \AA}$); micropores are pores with radii less than 0.01μ .

The development of porous structure in carbons as a consequence of activation reactions has been studied by several investigators. Dubinin and coworkers attempted to correlate the pore volume with total burnoff, but they had only partial success (18). Cameron and Stacey reported the removal of fine constrictions in pore openings in a carbon reacted with steam (19). Walker and Raats observed uniform surface reaction in electrode carbon rods, and increases in both macropore and micropore volumes (20). These earlier results indicated that pore development depended upon the character of the starting carbon, but did not succeed in giving quantitative interpretations of pore growth.

Recently there have been a number of papers on pore development in various carbons. Turkdogan et al., studying a metallurgical coke with rather little micropore area, found growth to occur principally by increase in macropore volume (21). The surface area of this coke increased with weight loss up to about 20%, then decreased. They concluded that none of the usual measurements of porous structure gives a direct measure of the effective surface area; i.e., the area which participates in oxidation reactions. They noted that in small carbon particles (less than 0.5-mm diameter) and at reaction temperatures below 1000°C , internal diffusion is not rate-limiting, yet they also concluded that reaction probably did not occur in micropores due to diffusion limitations.

Using microscopic examination, Kadlec et al. compared the pores produced by zinc dichloride activation with those produced by steam activation and concluded that zinc dichloride produced "bottle-shaped" pores, while steam produced "conical" pores which were larger at the pore mouth due to a higher activation rate at the pore mouth (22). Lamond et al. found that very small carbon-black particles, activated by oxygen, resulted principally in the growth of pores of less than $9 \text{ \AA}$ diameter (23).

Dubinin and Plavnik observed some growth of micropores in an anthracite coal activated with steam at 900°C (24). They found that as burn-off proceeded, larger micropores became more predominant. They concluded that

the size of crystallites determined the size of the pores and that the micropores grew larger as burning proceeded.

Chiche and coworkers found, in the activation of two carbonized coals with steam at 900°C , that the accessible surface area increased with carbon burn-off up to about 40% and then decreased (25). The surface area revealed by low-angle X-ray diffraction changed little, however, indicating that area present in the initial coke, but inaccessible to nitrogen, was being exposed by activation. They also found that pore volume increased up to 40 to 50% burn-off and that the volume increase was mostly in the micropores. They concluded that the development of large surface areas upon activation required the existence of a network of fine micropores in the starting material.

Donnett et al. studied the pore structure of a coal partially oxidized by oxygen at $225\text{--}325^{\circ}\text{C}$, carbonized at 650°C and then activated with steam at 900°C (25). They found that activation increased pore volume, especially micropore volume, and nitrogen surface area. The surface area increased due to greater accessibility of micropores and growth of micropores.

These several studies give a complex picture of pore development during activation. In most cases, pore diffusion seems not to have been important, though this was not often clearly established. In some cases accessible micropore volume increased, in others it changed little, but in all cases the surface area measured by gas absorption increased. The increase in surface area seemed in most cases to be due to burning which made accessible surfaces that were already present in the starting material.

The initial phase of the present work was to react carbonized coal with carbon dioxide at different conditions, to measure the reaction rates and the resulting porous structure, and to attempt to relate the results to initial porous structure and reaction conditions. These early results, combined with kinetic and diffusion data from the literature, led to the tentative conclusion that pore diffusion was a major factor in pore growth. In order to determine whether this was the case, it was necessary to have kinetic data for the specific carbon being studied and to have more information on diffusion in porous carbons.

The second phase of the work was a detailed study of the kinetics of carbon dioxide gasification of the carbonized coal. This was accompanied by measurement and analysis of diffusion characteristics of porous carbons. This work led to the conclusion that the reaction with carbon dioxide took place almost entirely in the macropores of the carbon wherein it was not diffusion controlled but was chemical-reaction-rate controlled. This work also indicated that diffusion was probably partially rate limiting in the micropores. A parallel study of pore growth in large cylinders of a highly pure graphite showed partial diffusion control of the reaction and pore growth due to end-burning of crystallites.

The next phase of the work was measurement of pore-growth characteristics of the carbonized coal over a much wider range of reaction conditions. This work showed that substantial changes in pore volume occurred when the carbon was heated using typical reaction conditions, except under a nitrogen or helium atmosphere such that no reaction took place. Although it was known that pore-volume changes occur due to heating (27), this result was surprising because the carbon had previously been heated in nitrogen to temperatures above the reaction temperature. This led to a study of activation at much lower temperatures (300-400° C) where volume changes due to heating alone were not significant. Air was used as the oxidant at the lower temperatures.

The final phase of this work was the analysis of the results in an attempt to quantitatively describe the observed pore-growth characteristics. It was not found possible to develop a theory to completely describe the observations. The theoretical aspects of this work will be presented in appropriate subsequent sections.

The balance of this report includes a description of materials and methods used, presentation of experimental observations, and analysis and discussion of the results.

SECTION IV

MATERIALS AND METHODS

Several different types of experiments and measurements were carried out in this work. These included: heat treatment of calcined coal, reaction of calcined coal over a wide range of temperatures and gas compositions, reaction of a purified graphite, diffusion measurements, and measurement of the porous structure of the various carbons used and produced. The experimental and measurement techniques, the properties of the material used and the ranges of the experimental conditions are described in this section.

Heat Treatment

The Elkol, Wyoming coal used as the principal raw material in this work had been calcined by heating to approximately 790°C before it was received. The activation reactions conducted in this work were most often carried out at temperatures above 790°C. It was found, as had been reported earlier (27), that in order to obtain consistent, reproducible reaction rate data, it was necessary to use as a starting material in the reaction a carbon that had been heated in inert gas to a temperature above the subsequent activation temperature. For this reason, batches of the calcined coal were heated in a muffle furnace under an atmosphere of flowing nitrogen to a temperature in the range 1100 to 1300°C for a period of from $1 - \frac{1}{2}$ to 16 hours. The heating was conducted for a long enough period so that the carbon reached a constant weight. A 5% weight loss was observed when the calcined coal was heated at 1100°C for 16 hours.

Activation System

Carbon samples were reacted with gases in the reaction system shown schematically in Figure 1. This reaction system was designed and constructed for this study. Slight modifications were made as necessary for specific purposes.

The reactor consisted of a Mullite tube (G) of 1-inch inside diameter and 33-inches long, heated by a vertical Globar furnace (N). The lower half of the tube was packed with porcelain chips to smooth the gas flow and heat the gas to the reactor temperature. At the bottom end of the reactor tube there were two openings, one for the gas inlet and the other for a thermocouple. For the reaction of granular, calcined coal, the sample container was a platinum basket (R), 3/4 -inch diameter and 3/4-inch high, with a 30-U. S. S. - mesh platinum screen as the bottom. The basket was suspended from a platinum wire which was connected to it through support wires. The basket was kept 1/4-inch above the tip of the thermocouple (J). The details of the

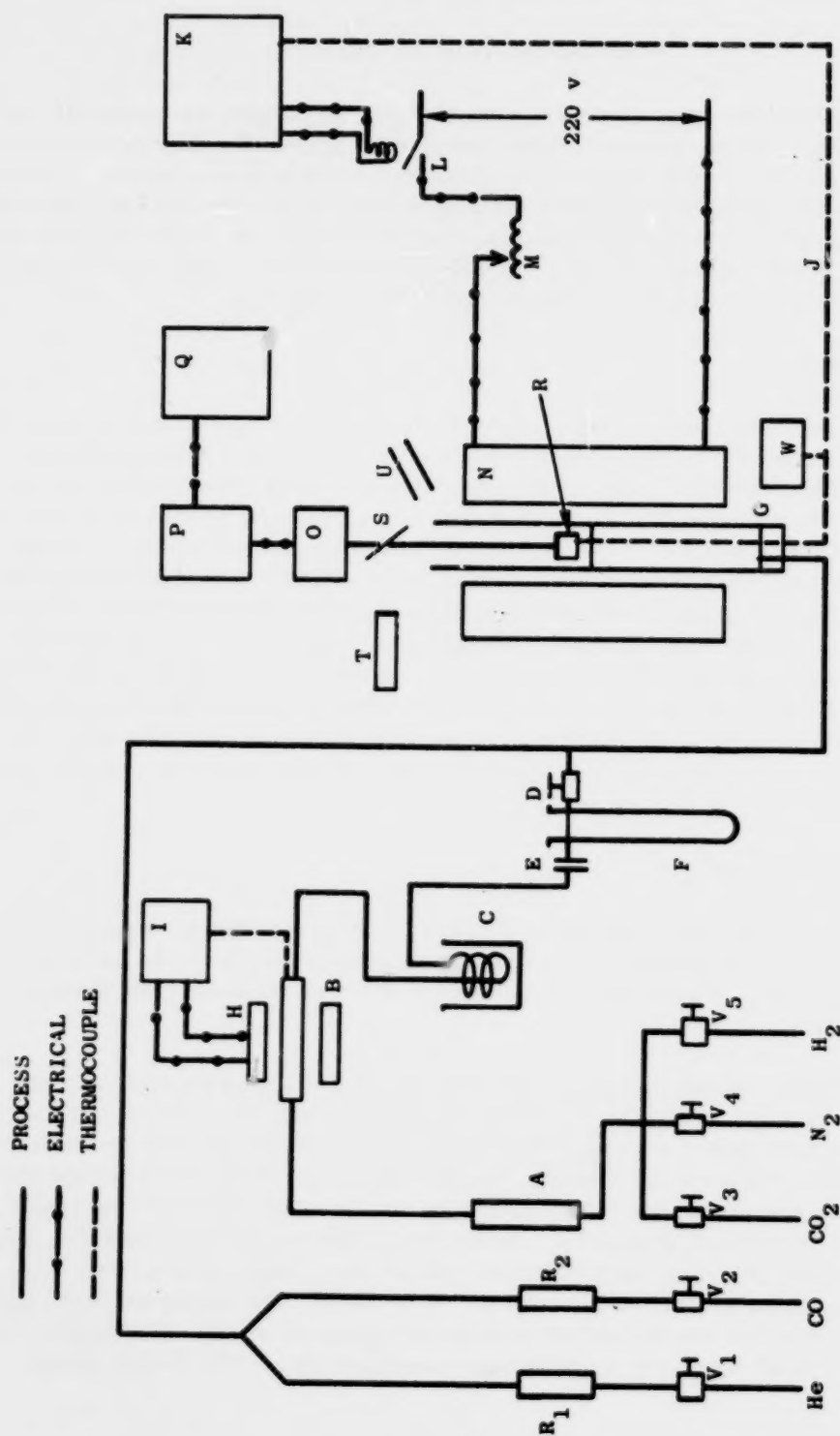


FIGURE 1. SCHEMATIC DIAGRAM OF REACTION SYSTEM

basket are shown in Figure 2. Graphite cylinders were suspended in the furnace on a nichrome wire through a center hole. The top and bottom of the cylinders were sealed with sauerisen ceramic cement. Samples of calcined coal ranged in weight from 100 to 500 mg. Smaller samples were used at higher reaction rates where the measured rate showed some dependence on sample size, apparently due to temperature gradients in the sample.

The temperature in the reactor tube was measured with a platinum vs. platinum-rhodium or a chromel vs. alumel thermocouple (J) extending from the bottom of the tube up to a point where the hot junction was about 1/2 inch above the surface of the packing. The temperature of the thermocouple was read on a Honeywell Model R7161B indicator-controller (K), or a Leeds & Northrup potentiometer (W). The thermocouple was calibrated against the melting point of reagent sodium chloride, 800.6° C.

The controller actuated a relay (L) which in turn controlled the power input to the furnace through a variable transformer (M). The actual sample temperature was measured by an optical pyrometer (T), via a mirror (S), when the temperature was above 700° C. The pyrometer reading was set with respect to the calibrated thermocouple. At lower temperatures the thermocouple was used to indicate the sample temperature, after it was calibrated by comparing its reading to that of another thermocouple actually inserted in the carbon bed and held in place by tying it to the support wires of the basket. When the carbon was heated with air, the sample temperature was greater than that of the thermocouple by less than 5° C, at 300° C, and by about 50° C at 400° C. Temperature values were read to $\pm 1^\circ\text{C}$ and varied during a given run by at most $\pm 3^\circ\text{C}$.

The sample-basket suspension wire was attached to one arm of an analytical balance (O). A Fisher Automatic Recording Balance Accessory (P) continuously balanced the weight and sent a signal to a Leeds and Northrup Millivolt Recorder (Q) which recorded the weight on chart paper. The balance was also used to obtain manually the initial, final and several intermediate weights of the sample. The balance was sensitive to 0.1 mg.

All the gases except air were supplied from commercial pressure cylinders. Air was obtained from the laboratory compressed air main. The gases were purified by passage through a silica gel adsorber (A) to remove moisture. Then all gases except air were passed through a bed of copper wool in a stainless steel tube (B) in an electric furnace (H). The temperature was controlled at 500° C by an on-off controller (I). The copper was used to remove oxygen from the gas stream. The gas was then cooled to room temperature by passing it through a coil which was placed in the cold water bath (C). The flow of gas was controlled by the valve (D) and was measured by measuring the pressure drop through a calibrated orifice (E) by means of a mercury manometer (F). When gas mixtures were used, the individual

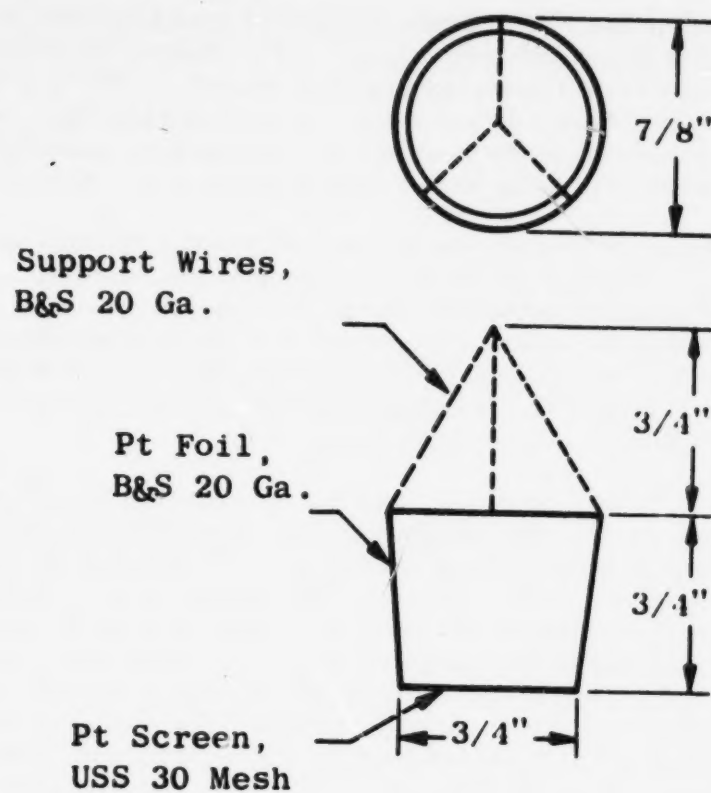


FIGURE 2. SAMPLE HOLDING BASKET

gases were metered through calibrated rotameters with the flow controlled by valves (V) to give the desired composition. The total flow was then measured by the orifice flow meter. A total gas flow of 100 cc/sec at STP was used. A mercury trap was inserted in the gas line downstream of the flow meter to prevent mercury from entering the hot furnace. The gases exiting the reactor tube were removed by a ventilating system (U) .

The procedure for a typical activation run will be described.

First, the ventilation blower (U) and the controller (I) were turned on. A small flow of hydrogen was sent through the stainless steel tube (B) to reduce any copper oxide formed during the previous run. After the reduction of copper oxide was completed, the hydrogen flow was stopped and the system was flushed with nitrogen.

The controller was set at the required furnace temperature, and the power to the furnace was turned on. When the furnace reached the set temperature, the temperature of the chromel-alumel thermocouple junction was measured by the optical pyrometer. In this way the optical pyrometer was calibrated in the vicinity of the desired temperature.

When the desired reaction temperature had been reached, the empty basket was suspended in the reactor tube from the analytical balance and was weighed. A nitrogen flow was started. The carbon sample was placed in the reactor basket. The basket was then suspended in the reactor tube, and the sample was heated at reaction temperature to constant weight. After this heating step, the nitrogen flow was stopped, and the sample and basket were weighed. The nitrogen flow was again started, and the controller was adjusted to the desired value. When the temperature of the sample reached the set value and was maintained constant, the flow of nitrogen was stopped and immediately the flow of reactant gases through the system was begun. The total gas flow in all the experiments was 100 cc/sec at STP. This flow rate was found to be well below the fluidization velocity of the carbon particles but essentially eliminated any exterior-film mass-transfer resistance.

The weight of the sample was recorded continuously. Since the total gas flow, gas composition and temperature were constant throughout the experiment, the weight loss recorded was only due to the loss of carbon by the chemical reaction.

When the sample weight had decreased by the desired amount, the flow of reactant gases was stopped, and the system was flushed with nitrogen. The power supply to the furnace was then shut off, and the sample was cooled to about 200°C in nitrogen. The nitrogen flow then was stopped, and the sample and basket were weighed.

The rate of reaction was calculated by the slope of the recorder trace and from the weight change as determined by initial, periodic and final weighings. The rates determined in these two ways were found to agree closely. The slope rates were used in the data analysis.

Diffusion Apparatus

An apparatus was constructed and used to measure apparent diffusivities in porous materials. No measurements were made on the carbons used in this work. Typical commercial activated carbons were used to determine the influence of porous structure on diffusion and the applicability of diffusion theories. The apparatus is described in detail in the thesis of Allen (28).

Property Measurements

The determination of the porous structure of carbons prepared from starting materials of differing structure under different reaction conditions was the main purpose of this work. The measurement of the structure of porous solids has been and continues to be the subject of intensive research. An excellent review of the current status of the subject has been presented recently by Dullien (29).

The measurement techniques used in this work for the determination of porous structure were "helium density", "mercury density", nitrogen-adsorption isotherms, and mercury penetration. Each method and the interpretation and analysis of the resulting information will be discussed.

The term "helium density" as used herein is defined as the weight of a solid sample divided by the volume of helium displaced by that sample. The helium-gas molecule has a diameter of approximately 2.30 Å (30). Helium, though very inert, has been reported to be slightly adsorbed on carbons, but the error in helium density resulting from adsorption at room temperature is probably not significant (31).

Helium densities were determined in a Numinco-Orr Model MIC-101-018 nitrogen-adsorption apparatus. A weighed sample of carbon was degassed by heating in a sample tube at 200-250°C and 0.0003-mm Hg pressure for about 24 hours. The sample was then exposed to helium at room temperature. The apparatus, method and calculations are described in the manufacturer's manual (32).

The term "mercury density" as was used herein is defined as the weight of a solid sample divided by the volume of mercury displaced by that sample. The mercury density was determined in the low pressure chamber of an Aminco Model 5-7108 mercury porosimeter. The apparatus, method and calculations

are described in the manufacturer's manual (33). A weighed sample was degassed in the vacuum chamber by holding the sample at room temperature for 10 to 15 minutes at a pressure of 0.005-mm Hg. The mercury density was calculated as the sample weight divided by the volume of mercury displaced at an absolute pressure of 1.7 psia, which corresponds to a pore radius of about 51μ (based on the Laplace equation and values discussed below). Thus, the mercury density as used herein is the mass of sample divided by the volume of the sample, including the volume of all pores with radii less than 51μ .

Gas adsorption, most commonly nitrogen, is the usual method for examining the microporous structure of materials. Adsorption at low relative pressures is used to determine surface area by the classical BET technique (34).

Nitrogen-adsorption measurements were conducted in a Numinco-Orr Model MIC-101-018 apparatus at liquid-nitrogen temperature. The apparatus and methods are described in the manufacturer's manual (32). The BET surface area is found to depend somewhat on the type of gas molecule due to different molecular sizes (29).

As the pressure is increased in a nitrogen-isotherm experiment, the phenomenon of capillary condensation begins to occur in very small pores, and further increases in pressure cause it to occur in still larger pores. Thus, nitrogen isotherms at high relative pressure may be interpreted to give cumulative pore volume as a function of pore size. To do so requires several assumptions. First, a pore model (i.e., a shape) must be assumed. The usual practice is to assume cylindrically shaped pores, even though microscopic examination usually indicates irregularly shaped pores (29). When this is assumed, the Kelvin equation

$$\ln p/p_o = \frac{-2\sigma v \cos \beta}{r_K RT}$$

may be applied (29). The properties σ , v and $\cos \beta$ are taken as the bulk properties of liquid nitrogen, and the Kelvin equation becomes

$$r_K = -10/\ln(p/p_o).$$

The calculations must be corrected for the fact that condensation occurs within the pores that already have gas adsorbed on their surface, thus reducing the radius. This is done by the "t-method", using averaged values of t from several authors (35). The actual pore radius, r , is then the Kelvin radius, r_K , plus the appropriate t . The pore volume corresponding to a calculated radius interval is taken as the total amount of nitrogen desorbed, less the uncondensed amount desorbed, divided by the density of liquid nitrogen.

Nitrogen-adsorption isotherms in porous carbons typically exhibit hysteresis;

i.e., the adsorption and desorption branches do not coincide. This was found with the carbons used in this study and, as is the usual practice (29), the desorption isotherm was used in the calculations. Finally, in very small pores, that is those less than about 16 Å radius, it cannot reasonably be assumed that a liquid phase is formed since the dimensions of the pore are comparable to the dimensions of the nitrogen molecule; thus, volume calculations become very tenuous for calculated radii of less than about 16 Å. The nitrogen isotherms are useful for calculations up to pore radii of 150 to 200 Å (36).

The preceding discussion emphasizes the fact that pore volumes obtained from nitrogen-adsorption data are not absolute quantities but are subject to limitations inherent in the several assumptions made in the calculations. Micropore-volume distributions must be considered, then, relative values. As such they are useful, however, especially for making comparisons of pore volumes between similar materials, such as the carbons studied in this work.

Mercury penetration into porous solids under pressure is useful for determining macropore characteristics. Progressively higher pressures are required to force mercury into pores of smaller and smaller radius.

An Aminco Model 5-7108 mercury porosimeter was used for these measurements. This instrument is capable of a maximum pressure of 15,000 psia, corresponding to a radius of about 0.006 μ (60 Å). In the later stages of this work, a Wallace and Tiernan gauge was substituted for the high-pressure gauge supplied by the manufacturer to allow better accuracy.

It is necessary to make several assumptions in order to convert data for mercury penetration versus pressure into pore volume as a function of pore size. The important assumptions are: a pore model (i.e., a shape) for which straight cylindrical pores are usually assumed; and that the properties of mercury in the pores are the same as the bulk properties.

For cylindrical pores, the radius and pressure are related by the Laplace equation (37)

$$r = \frac{-2\sigma \cos \theta}{p}$$

The properties of mercury used were $\sigma = 475$ dynes/cm and $\theta = 130^\circ$ (38). Substituting these values into the previous equation and converting units gives

$$r = \frac{88.6}{p}$$

where the radius, r , is in microns and the pressure, p , is in psia.

The mercury-porosimeter method attributes all the pore volume penetrated

between two pressures to pores with radii in the range calculated from those two pressures by the preceding equation. If the material contains "ink bottle" shaped pores (that is, volumes of a certain size accessible only through openings of smaller radius), all the corresponding volume will be attributed to the smaller radius. Dullien has shown recently that this problem can lead, at least in the case of a porous solid produced by compacting a powder, to a mean radius (as determined by mercury porosimetry) that is nearly a factor of ten lower than that determined by a new microscopic technique (29). This points out that mercury-penetration results yield relative, rather than absolute, pore-volume distributions. Again, however, such distributions are useful for comparing similar materials such as the carbons studied in this investigation.

The usual interpretations were assumed in this work to use nitrogen-adsorption data to calculate surface area and cumulative micropore volumes at various radii (32), and to use mercury-penetration data to calculate cumulative macropore volumes (33). A digital computer program, in FORTRAN IV, was written to calculate the micropore-volume distributions from the raw nitrogen-adsorption data.

Materials

The raw material used for most of the activation studies was the calcinate of a sub-bituminous coal supplied by the FMC Corp. from the Elkol Mine, Kemmerer, Wyoming. The calcinate was produced from the as-mined coal by grinding, charring by rapid heating to about 480°C and calcining by rapid heating to about 790°C. Two different batches of calcinate were used during the course of this work, but no significant differences were found in their properties or behavior.

The compositions of the as-mined coal and the calcinate, as given by FMC Corp., are given in Table 1.

Table 1 - PROXIMATE ANALYSIS OF COAL AND CALCINATE

	<u>Coal</u>	<u>Calcinate</u>
Moisture, %	14.1	0.0
Volatile, %	35.6	4.5
Fixed Carbon, %	46.7	89.2
Ash, %	<u>3.6</u>	<u>6.3</u>
Total, %	100.0	100.0

The ultimate analysis, also supplied by FMC Corp., is given in Table 2.

Table 2 - ULTIMATE ANALYSIS OF COAL AND CALCINATE (DRY BASIS)

	C	H	N	S	O	Ash	Total
Coal, wt %	70.8	5.06	1.09	0.80	18.24	4.01	100.0
Calcinate, wt %	89.6	1.27	1.22	0.43	1.66	5.82	100.0

The calcinate, as shipped, was screened and the less-than-16 but greater-than-20 USS-mesh fraction (nominal particle size 1.0 mm) was used throughout this work, except in a few cases for which different mesh sizes are denoted. Batches of this fraction of calcinate were heat-treated in nitrogen within a temperature range of 1100-1300°C before use for most of the activation studies. This will be discussed more fully when the results are presented. By means of heat treatment and partial activation, starting materials for further activation were prepared which had different initial porous structures.

A portion of this work involved activation of a graphite. The graphite used was obtained from the Pure Carbon Company. It was their DS-12 grade with a reported porosity of 20 volume percent. Pure Carbon Company reported that the graphite contained a maximum ash content of 0.001 percent. The graphite was in the form of cylinders, 19 mm in diameter, 25.4 mm in length and with a 6-mm hole through the center.

Diffusion properties were measured on two commercial activated carbons. One was a North American Carbon, Inc., G-352 activated carbon with a porosity of 0.598, in pellets 4.67-mm diameter by 8.1-mm long. The second was a Chemetron Chemical Corp., G-32E activated carbon with a porosity of 0.508, in pellets 4.45-mm diameter and 6.51-mm long. More detailed structural data have been reported (28).

Commercial bottled gases were used in this investigation. Carbon dioxide, nitrogen, helium, and hydrogen were supplied by the Natural Gas Company, Denver, Colorado. Carbon monoxide was supplied by the Matheson Company, Inc. The compositions of these gases, as stated by the suppliers, were as follows:

N ₂ :	99.98 % N ₂ , 0.02 % C ₂ , Dew point - 70 °F
He:	99.998% He, 0.002 % C ₂
H ₂ :	99.998% H ₂ , 0.0004% O ₂ , 0.0004% N ₂ , Dew point - 67 °F
CO ₂ :	99.63 % CO ₂ , 0.05% O ₂ , trace combustibles, Dew point - 88°F
CO:	99.5% minimum CO

The gases were purified as described earlier. Air was taken from the laboratory compressed air supply and was passed through a cotton filter to remove oil, then through a silica gel bed to remove moisture.

Calculation of Properties

Throughout this report all properties that are based on a unit mass of carbon will be presented on the basis of a unit mass of starting material. Starting material is defined as the carbon to be reacted, with zero weight fraction removed by reacting gas, but after any weight change due to loss of volatiles. Properties measured per g of sample after weight loss due to reaction were converted to the corresponding values for one g of starting material by multiplying these properties by the fraction of the original weight remaining after reaction. For example, suppose 10% of the weight of starting material was removed by reaction (10% burnoff), then one g of starting material would yield 0.9 g of reacted sample. If the pore volume of the reacted sample was, say, 0.5 cc/g, then the pore volume was $0.5 \times 0.9 = 0.45$ cc/g of starting material. Putting all the values on the basis of starting material makes it possible to compare directly the properties of materials which have been reacted to different extents of burnoff.

The total pore volume, V_p , in a sample was determined, in cc/g, from the mercury and helium densities. The mercury density is the mass of carbon, divided by the volume of carbon plus the volume of all pores with radii less than 51μ . The reciprocal of the mercury density is thus the volume of carbon, plus pores, per unit mass. The reciprocal of the helium density is the volume of carbon not penetrated by helium, per unit mass. The reciprocal of the mercury density, minus the reciprocal of the helium density, is thus the volume penetrated by helium but not by mercury. Hence,

$$V_p = \frac{1}{\rho_{Hg}} - \frac{1}{\rho_{He}} \quad (1)$$

This then gives the volume of all pores ranging from those accessible to, and penetrable by, helium up to those of 51μ radius.

The porosity, ϵ , is closely related to the total pore volume. The porosity is the volume of pores, divided by the volume of carbon plus the volume of pores. It is thus given by

$$\begin{aligned} \epsilon &= \left(\frac{1}{\rho_{Hg}} - \frac{1}{\rho_{He}} \right) / \frac{1}{\rho_{Hg}} \\ &= 1 - \rho_{Hg} / \rho_{He} \end{aligned} \quad (2)$$

Porosity was not converted to a starting material basis because it is dimensionless.

Mercury-penetration data were used to calculate macropore volume and macropore-volume distribution. Macropores are herein defined as pores with radii greater than 0.01μ ($100 \text{ \AA}$). The dividing line between macropores and micropores is somewhat arbitrary, but this value was found convenient since the carbons which were studied exhibited bimodal pore distributions with large volumes in pores with radii greater than 0.01μ , virtually no volume between 0.01μ and 0.005μ radius, and then pore volume again in pores less than about 0.005μ ($50 \text{ \AA}$) radius. The macropore volume was thus taken as the volume penetrated by mercury at a pressure corresponding to an 0.01μ pore radius; i.e., a pressure of about 8860 psia.

Cumulative macropore volumes as a function of radius were determined from mercury penetration at various pressures, using calculations based on the Laplace equation as discussed earlier. That is, for any given pressure and corresponding radius, the cumulative volume of pores with radii greater than that radius is equal to the total volume of mercury that has penetrated the sample under that pressure. Results for cumulative volume versus radius were differentiated graphically or numerically to give volume-distribution curves.

Total micropore volume was calculated as the total pore volume minus the macropore volume. Cumulative volumes of micropores having radii greater than a given radius were calculated from the nitrogen-desorption isotherms via the Kelvin equation as described earlier. The cumulative volume data were graphically or numerically differentiated to give volume distribution by radius.

Surface area was determined from nitrogen-adsorption data by the usual BET method (34).

SECTION V

RESULTS

The results of the experiments will be presented in this section. The original, raw data may be found in the several theses prepared as portions of this work (28, 35, 39, 40, 41, 42, 43).

Kinetics and Diffusion

Rate data obtained from the reaction of calcined coal with carbon dioxide were analyzed to determine the appropriate rate expression and rate coefficients. The effect of temperature on rate was investigated to establish the rate-controlling mechanism of the reaction.

Several interesting features of the carbon-carbon dioxide reaction should be noted. It was observed with the calcined coal, as with other carbons (48), that during the initial stages of reaction, the rate increased slowly with time up to 5 to 10% burnoff. This phenomenon is usually attributed to the exposure of reactive sites resulting from the removal of carbon (49). The reaction rate then reached a constant value that did not change as the weight of carbon decreased and the surface area of the carbon increased. Because of this, reaction rates are expressed as the percent decrease in initial weight per hour during the constant rate period. This is, again, a common observation and is attributed to the reaction occurring at discrete, active sites which are not changed by the reaction (49). At high degrees of burnoff, usually those greater than 50% of the initial weight, the reaction rate may decrease (35).

In the calcined coal used in this work, it was found that nearly all of the observed weight-loss of carbon occurred in the macropores, even though the vast majority of the surface area was in the micropores (this will be demonstrated and discussed later). This again confirms that the reaction rate is not directly related to total surface area. It further indicates that the controlling mechanism of the observed reaction rate is essentially entirely that associated with the macropores.

Reaction rates of calcined coal with carbon dioxide were measured over a temperature range from 780 to 961°C in gas atmospheres containing from 30 to 100 mol% carbon dioxide, from 0 to 20 mol% carbon monoxide, and from 0 to 70 mol% inert diluent (either nitrogen or helium) at 620 to 630-mm Hg total pressure. The measured rates ranged from 1.4 to 106% per hour.

One observation was that heat-treating the calcinate had a very significant effect on the rate of reaction. For example calcinate, heated for 1.5 hrs in

nitrogen at 1300°C, reacted at 31.4%/hr with carbon dioxide at 875°C; whereas calcinate, heated 16 hrs at 1100°C, reacted at 14.5%/hr with carbon dioxide at 875°C (42). This effect was not studied in detail. However, as will be shown later, pore-volume changes also occurred upon heat treatment. It seems likely that the form and reactivity of the carbon was changed by heating, as has been reported (27); also pore volume and surface-area changes occurred which may have affected reactivity. The rate data plotted and discussed here are for calcined coal heated at 1100°C for 16 hrs in nitrogen. Data for other heat-treatment conditions were analyzed, but gave different rate coefficients.

If the log of the reaction rate is plotted against the reciprocal of absolute temperature, as is illustrated in Figure 3, it is found that below some temperature (about 880° C in this case) a straight line is obtained, and above that temperature there is curvature. Such a result has been observed earlier, and the curvature has frequently been interpreted as being due to the onset of intra-particle diffusion control of the reaction rate (50). It has also been pointed out that this inference is weak in the case of a complex reaction such as carbon gasification (50). Thus, further investigations were conducted to determine whether diffusion was rate limiting.

Table 3 presents the observed rates of the carbon-carbon dioxide reaction with different gas-flow rates and different particle sizes. The average particle size was varied from 1.0 to 0.62 mm and the Reynolds number was changed from 32 to 64.

Table 3 - EFFECT OF PARTICLE SIZE
AND GAS FLOW RATE ON REACTION RATE

Temperature, ° C	Particle Size, USS mesh	Gas Flow, cc/sec, STP	Rate, %/hr
920	-16 +20	100	47.5
920	-28 +30	100	48.3
920	-16 +20	50	47.1
961	-16 +20	100	100.
961	-20 +28	100	104.
961	-20 +28	50	106.
961	-28 +30	100	104.

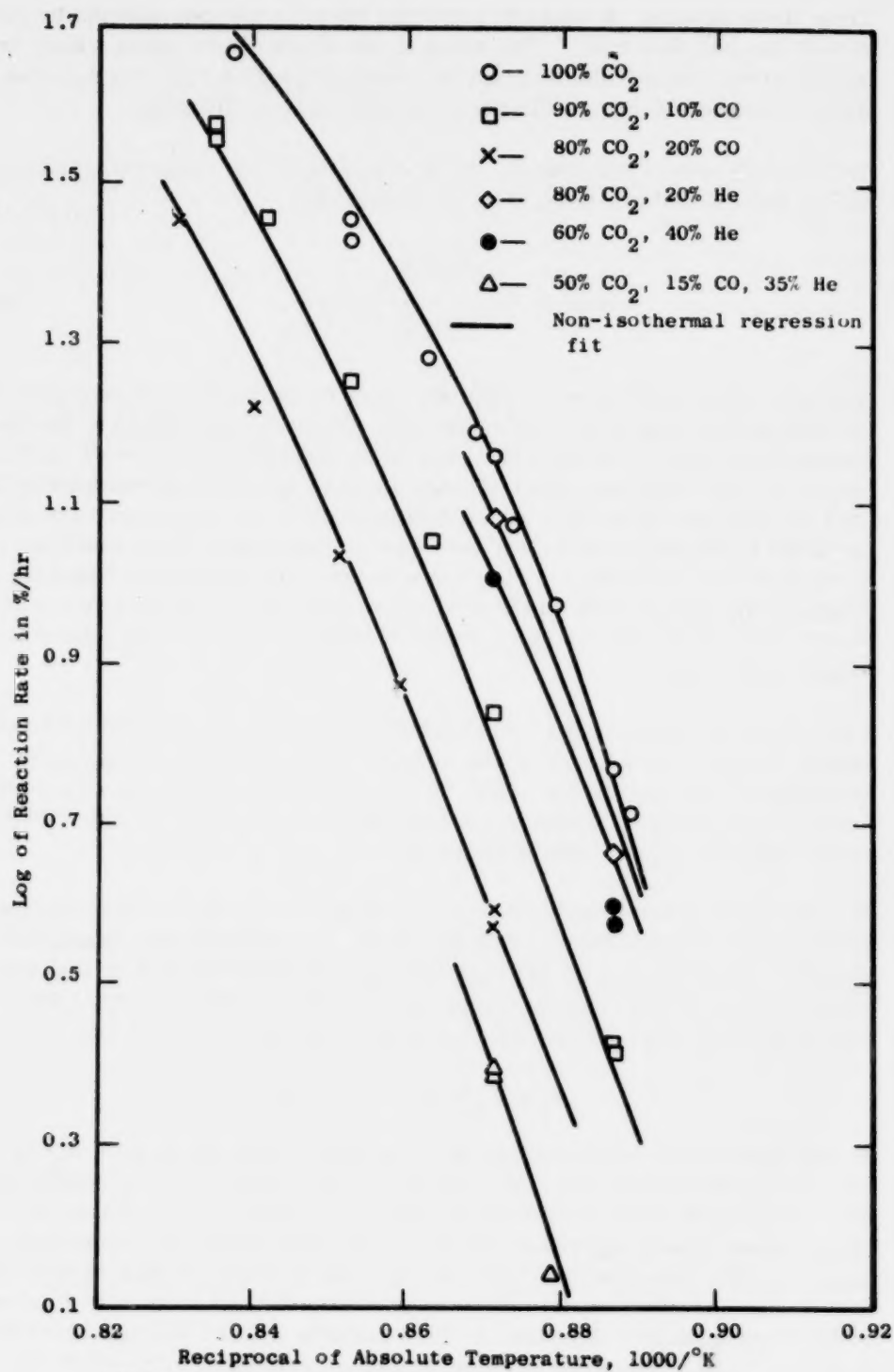


FIGURE 3. LOG OF REACTION RATE VERSUS RECIPROCAL OF ABSOLUTE TEMPERATURE

From these results, it could be seen that the rate was not affected by particle size or the gas flow rate. The rates at one temperature agree within experimental error, thus indicating that the overall reaction rate was not even partially controlled by pore diffusion or by external gas diffusion.

As a further test of this result, the rate constants for temperatures below 880°C were calculated using the rate expression,

$$\text{Rate} = \frac{k_1 p_{\text{CO}_2}}{1 + k_2 p_{\text{CO}} + k_3 p_{\text{CO}_2}} \quad (3)$$

as will be discussed below. Then the rates at the higher temperatures were calculated from equation 3 using the rate constants obtained from the lower temperature data. The average, absolute, percent difference of 7.2% between the calculated and observed rates at the higher temperatures was less than the average, absolute, percent difference of 10.1% between the calculated and observed rates for the lower temperature data from which the constants had been calculated. Thus the reaction rate expression fitted the high temperature data as well as the low temperature data with the same rate constants, indicating that the same reaction mechanism holds over the entire temperature range.

From these results it was concluded that the overall reaction rate was controlled by the rate of the chemical reaction over the entire temperature range investigated and that the curvature in the plot of log of reaction rate versus reciprocal of absolute temperature was due to the form of the rate equation, rather than the onset of the diffusion control.

Several rate equations have been proposed for the carbon-carbon dioxide reaction (42). Eight different rate expressions, including two empirical power models, were fitted to all the reaction rate-temperature data to find which would fit best and to evaluate the parameters in the models (42). When this was done, the rate coefficients, k_i , were taken to be of the form,

$$k_i = A_i (\exp (-\Delta E_i/RT)) \quad (4)$$

so that data for all temperatures were included. For example, A_1 is the pre-exponential factor and ΔE_1 the activation energy for rate coefficient k_1 . The calculations were done using a digital computer program based on a non-linear least-square algorithm (44, 45) which minimized the normal sum-of-squares. The result of this was that equation 3 fitted the data as well or better than any other model and with fewer adjustable parameters than equally well-fitting models. Equation 3 fitted the data with an average absolute error of 7.2%, compared to an estimated experimental error of 8.5%. Thus,

equation 3, the generally accepted rate expression for the carbon-carbon dioxide reaction (51), was found to fit the present data satisfactorily (42). The fit for various temperatures and gas compositions is shown in Figure 3.

The pre-exponential factors and the activation energies obtained for the rate coefficients of equation 3 are shown in Table 4.

Table 4 - RATE-COEFFICIENT PARAMETERS FOR
REACTION OF CALCINED COAL WITH CARBON DIOXIDE
CALCINATE HEATED AT 1100°C FOR 16 HRS IN NITROGEN

Quantity	Value
Temperature, °C	852 to 961
p_{CO_2} , atm	0.83 to 0.25
p_{CO} , atm	0.00 to 0.17
A_1 , %/hr-atm	4.9×10^{10}
E_1 , kcal/g mol	48.5
A_2 , atm ⁻¹	2.5×10^{-14}
E_2 , kcal/g mol	-78.5
A_3 , atm ⁻¹	2.3×10^{-24}
E_3 , kcal/g mol	-124.0

Thus, it was concluded that for the calcined coal used, the observed overall reaction rate was controlled by the rate of chemical reaction, and not by diffusion, at temperatures as high as 961°C and rates as high as 106%/hr. It was further concluded that the rate could be represented by equation 3 with the rate constants given as a function of temperature by equation 4. The actual values of the rate constants were found to depend upon the heat treatment of the calcinate prior to reaction (42).

The foregoing results show that the observed rate of reaction is chemical reaction limited. However, since the reaction was found to occur almost entirely in the macropores, the rate-limiting mechanism in the micropores was not clearly established. That is, the micropores, even with their far greater surface area than the macropores, seem to react very slowly. Is

this because diffusion strongly inhibits reaction in the micropores, or is it that the micropore surface is inherently less reactive? This question cannot be answered unambiguously, but the following analysis gives an indication that diffusion is partially limiting in the micropores.

The reaction-kinetic results developed above, plus information on the diffusion characteristics of activated carbons (28), may be used to estimate effectiveness factors for various pore sizes. The effectiveness factor is the ratio of the reaction rate, considering diffusion, to that without diffusion and is thus indicative of the extent of diffusion control (46).

Measurements of unsteady-state diffusion coefficients on two activated carbons, as well as other porous solids, showed that the effective diffusivity in the solids always lay between the extremes of Knudsen diffusion and bulk diffusion, and they were rather well predicted by the theoretical model of Otani et al. (47), provided adsorption did not occur (28). When adsorption did occur, as with carbon dioxide and carbon monoxide on carbon, the effective diffusivities tended to be substantially higher than those predicted by the model (28). In any event, the predominant diffusion mechanisms appear to be Knudsen diffusion in the micropores and ordinary diffusion in the macropores.

Effectiveness factors for macropores were estimated by the method of Roberts and Satterfield (46), using the kinetic data from above and using the bulk diffusivity for macropores and the Knudsen diffusivity for the micropores. The estimated effectiveness factors are summarized in Table 5.

Table 5 - EFFECTIVENESS FACTORS

Temperature, °C	Effectiveness Factor		
	Macropore	Micropore 20 Å 10 Å	
852	1.0	0.9	0.8
872	1.0	0.8	0.7
920	1.0	0.75	0.6
961	0.99	0.75	0.6

The macropore-effectiveness factors support the previous conclusion, that is that diffusion is not rate limiting up to 961° C; although they suggest that, at that temperature, diffusion may be just beginning to influence the rate. The micropore-effectiveness factors, on the other hand, suggest that diffusion is at least partially rate limiting in the micropores over the temperature range 852 to 961° C and that it may be rather strongly rate limiting in pores with radii less than 10 Å. This partial diffusion limitation probably does not

fully explain the relatively slow growth of micropores. This will be further discussed later.

In the reaction of graphite cylinders of 0.75 inches diameter with carbon dioxide at 1030° C, which resulted in reaction rates of about 5%/hr, diffusion effects were noted. The small apparent activation energy of the reaction, 66 kcal/g mol, plus less increase in pore volume as one moved radially inward from the outside surface to the center of the cylinder, established that diffusion was limiting the internal rate of reaction (40). Some growth of small pores was observed in the graphite, nonetheless. The graphite, however, contained essentially no micropores, so it is likely that diffusion rate was not affected by pore size.

The very great differences in reaction rates between the calcined coal and the purified graphite should be noted. Whereas the calcined coal reacted with carbon dioxide at a rate of about 100 %/hr at 960° C, the graphite reacted at 5 %/hr at 1030° C. Such vast differences in reactivity between graphite and the more amorphous and impure forms of carbon are commonly observed (51). The reasons are probably that the carbon in the graphitic crystal structure is more stable and less reactive than amorphous carbon and, perhaps even more importantly, that many mineral impurities catalyze the oxidation of carbon (51). The catalytic effect of many metals and metal compounds is well recognized (52).

Effects of Heat Treatment

The calcined coal, as obtained, was screened and then heated in batches in nitrogen. This was necessary in order to obtain consistent, reproducible reaction-rate data (27, 35). As this study progressed, it was found that heating in nitrogen affected the rate of reaction when the carbon was subsequently reacted with oxidizing gases and that heating in nitrogen also affected the porous structure of the carbon. Some comparative rates after different heat treatments were already mentioned. These phenomena were not studied in detail. However, some results on changes in pore structure due to heating will be presented here.

Experiments were conducted to determine the effects of heating in either nitrogen or helium on the pore volumes of the carbon. The results are presented in Table 6. The first row in Table 6 shows the properties of the raw calcinate as received. The last three rows show the properties of the raw calcinate after heating in nitrogen at temperatures up to 400° C. The results show that essentially no change in pore structure occurred due to heating in nitrogen up to 400° C.

Table 6 - PORE-VOLUME CHANGES DUE TO HEATING

Starting Material	Temperature, °C	Gas Atmosphere	Time of Heating, Hr	Weight Change, %	Pore Volume, cc/g of starting material		
					Total	Macro-pore	Micro-pore
Raw Calcinate, unheated	--	--	--	--	.423	.278	.145
Raw Calcinate	1100	Nitrogen	16	5.	--	.455	--
Raw Calcinate	1200	Nitrogen	16	5.	.473	.431	.042
Raw Calcinate	1300	Nitrogen	1.5	--	.580	.470	.110
Calcinate Heated to 1100°C	880	Helium	1.5	0.0	--	.565	--
Calcinate Heated to 1200°C	900	Helium	10	0.0	.593	.560	.033
Calcinate Heated to 1200°C	900	Nitrogen	10	0.0	.458	.376	.082
Raw Calcinate	400	Nitrogen	1 to 2	4.	.425	.278	.147
Raw Calcinate	350	Nitrogen	1 to 10	3.6	.424	.278	.146
Raw Calcinate	300	Nitrogen	1 to 24	3.	.411	.271	.140

This was true even though there was some weight loss due to devolatilization. This result was further substantiated by the fact that the macropore cumulative volumes were essentially unchanged (43).

On the other hand, heating the raw calcinate in nitrogen to temperatures of 1100 to 1300°C did change the pore structure. The total pore volume increased, the macropore volume increased and the micropore volume decreased. It is interesting to note that all the measurable changes were in mercury

density and mercury penetration; the helium density remained constant at 1.64 to 1.66 g/cc in all these cases (43). The constant helium density indicates that closed pores inaccessible to helium were not being opened, nor were pores originally open being closed and made inaccessible to helium. Apparently the loss of micropore volume was due either to expansion of micropores to become macropores or to complete collapse of micropores. It is also possible that the heating changed the surface properties so as to change the wetting characteristics of mercury, but there is no other evidence for this. It is not clear why the sample heated to 1200°C showed less micropore volume than that at 1300°C, although the heating time of the former was considerably longer.

Further experiments were done in which calcinate that had been heated in nitrogen to 1100 or 1200°C was reheated in nitrogen or helium at temperatures of 880 or 900°C. It was supposed that no changes would occur upon reheating since the material had already been heated to a higher temperature. It was found, however, as shown in Table 6, that rather major changes in pore volume occurred upon reheating. This was especially true when the gaseous atmosphere was helium rather than nitrogen. It should be noted that in these cases there was no detectable weight loss and no change in helium density. It should also be noted that the rate of heating in the reheating process was much greater than that of the original heating. Again, the reasons for these changes are not clear, but the fact that they occur at temperatures as low as 880°C could make the interpretation of pore-growth experiments at higher temperatures more difficult since it must be recognized that pore-volume changes might occur which are not a direct result of reaction. Apparently either thermal shock or carbon mobility at higher temperatures caused the observed volume changes due to heating (27).

A significant result of these observations is that heating in inert atmospheres tends to change the porous structure and in particular tends to reduce both the amount of micropore volume and the micropore fraction of the total pore volume. This is an undesirable change if the objective is to make a high-surface-area activated carbon. This may explain why it is stated that chars heated above 700 to 800°C do not produce active carbons (7).

Effects of Activation

Calcined coal samples were activated at some 34 different sets of conditions. Table 7 contains a summary of the results obtained, except for the cumulative macropore and micropore volumes and the volume distributions which will be presented below. For the last two reaction conditions in Table 7 the starting material had already been partially reacted and the pore volumes and surface areas presented are based upon one g of that starting material. These same results are presented in Table 7a, but converted to the basis of one g of original unburned calcinate.

Table 7 - RESULTS OF ACTIVATION OF CALCINED COAL

REACTION CONDITIONS	PERCENT BURNOFF	ρ_{Hg} , g/cc	ρ_{He} , g/cc	Porosity, ϵ	PORE VOLUME cc/g of starting material		SURFACE AREA, m ² /g of start- ing material
					Total	Macropore	
Air, 300°C	0 ¹	.986	1.661	.406	.411	.277	.134
	2	.970	1.664	.418	.423	.291	.132
	5	.949	1.669	.431	.431	.290	.141
	7	.921	1.742	.471	.476	.325	.151
	8	.927	1.790	.478	.478	.294	.185
	9	.898	1.799	.500	.509	.328	.181
	10	.901	1.830	.508	.507	.301	.206
	12	.868	1.848	.530	.537	.315	.222
	0 ¹	.976	1.662	.414	.424	.280	.144
	1.4	.968	1.667	.420	.428	.306	.122
	4.4	.937	1.678	.441	.452	.322	.132
	5	.953	1.677	.432	.431	.289	.143
Air, 350°C	6.4	.906	1.770	.489	.504	.342	.162
	8	.921	1.825	.493	.494	.302	.192
	8.4	.870	1.833	.526	.555	.348	.207
	10	.889	1.861	.524	.532	.319	.215
	12	.845	1.875	.550	.571	.340	.232
	0 ¹	.975	1.663	.415	.426	.284	.142
	1	.964	1.669	.423	.435	.319	.116
	4	.925	1.680	.449	.467	.327	.140
	5	.941	1.680	.440	.441	.293	.148
	6	.890	1.763	.495	.524	.350	.174
	8	.878	1.847	.525	.531	.335	.216
	10	.875	1.883	.536	.548	.325	.223
	12	.829	1.899	.564	.600	.361	.239
Air, 400°C	0 ¹	.975	1.663	.415	.426	.284	.142
	1	.964	1.669	.423	.435	.319	.116
	4	.925	1.680	.449	.467	.327	.140
	5	.941	1.680	.440	.441	.293	.148
	6	.890	1.763	.495	.524	.350	.174
	8	.878	1.847	.525	.531	.335	.216
	10	.875	1.883	.536	.548	.325	.223
	12	.829	1.899	.564	.600	.361	.239
	0 ¹	.976	1.662	.414	.424	.280	.144
	1.4	.968	1.667	.420	.428	.306	.122
	4.4	.937	1.678	.441	.452	.322	.132
	5	.953	1.677	.432	.431	.289	.143

Table 7 (cont.):

REACTION CONDITIONS	PERCENT BURNOFF	ρ_{Hg} , g/cc	ρ_{He} , g/cc	Porosity, ϵ	PORE VOLUME, cc/g starting material		SURFACE AREA, m ² /g starting material
					Total	Macropore	
80% carbon dioxide + 20% Helium, 872°C	O ²						28
	15					.445	47.
	30					.637 .725	48.
80% carbon dioxide + 20% carbon mon- oxide, 888°C	15					.655	45.
	30					.730	46.
Carbon diox- ide, 800°C	O ³						38.
	15	.84	1.64	.49	.58	.47	46.
	30	.69 .62	1.79 1.93	.61 .68	.75 .77	.66 .70	43.
Carbon diox- ide, 900°C	O ³						38.
	15	.84	1.64	.49	.58	.47	52.
	30	.74 .62	1.83 1.89	.59 .67	.68 .76	.58 .65	59.
Carbon diox- ide, 900°C	O ⁴						54.
	15	.69	1.79	.61	.89	.78	70.
	30	.63 .52	1.84 2.00	.66 .74	.88 .99	.79 .91	84.
Carbon diox- ide, 900°C	O ⁵						61.
	15	.62	1.93	.68	1.10	1.00	91.
	30	.53 .47	1.87 1.97	.72 .76	1.15 1.13	1.06 1.03	95.

1. Starting material was raw, calcined coal after heating to constant weight at reaction temperature.
2. Starting material was calcined coal after heating in nitrogen for 16 hrs at 1100°C.
3. Starting material was calcined coal after heating in nitrogen for 1½ hrs at 1300°C.
4. Starting material was calcined coal, heated 1½ hrs at 1300°C, then reacted to 15% burnoff with carbon dioxide at 800°C.
5. Starting material was calcined coal, heated 1½ hrs at 1300°C, then reacted to 30% burnoff with carbon dioxide at 800°C.

Table 7a - TWO-STEP BURNING RESULTS ON
BASIS OF ORIGINAL UNBURNED CALCINATE

ON BASIS OF UNBURNED CARBON ⁶					
REACTION CONDITIONS	PERCENT BURNOFF	PORE VOLUME, cc/g of unburned calcinate			SURFACE AREA, m ² /g of unburned calcinate
		Total	Macro	Micro	
Unburned Calcinate	0	.58	.47	.11	38.
Carbon diox- ide; 15% burn- off at 800 °C, remainder at 900 °C	27.8	.75	.67	.08	60.
	40.5	.84	.77	.07	71.
Carbon diox- ide; 30% burn- off at 800 °C, remainder at 900 °C	40.5	.81	.74	.07	64.
	51.	.79	.72	.07	67.

6. Original starting material was calcined coal heated in nitrogen for 1½ hrs at 1300 °C .

It can be seen in Table 7 that as the burnoff of carbon increased, the mercury density of the carbon decreased. It has been shown (see appendix 1 for development of equations) that if all the burning occurs on the interior surface of the carbon particles, the ratio of sample-to-initial mercury density, $\rho_{\text{Hg}}/\rho_{\text{Hgo}}$, should be a linear function of the fraction of carbon remaining, $1 - f$ (where f is the fraction burnoff), with a slope of -1 . The data are plotted in Figure 4 and show that indeed the results follow the theoretical line for a wide range of gas compositions, burnoffs and temperatures. There is some scatter but the trend is quite clear, indicating that the removal of carbon during activation was substantially all from the interior of the particles, creating new void volume.

The helium density showed a distinctly different trend, as shown in Figure 5. Up to 4 to 5% burnoff, the helium density did not change; then between about 5 and 12% burnoff, the helium density rose sharply. At burnoff higher than 12%, the helium density increased slowly. There is a rather sharp decrease in helium density between 12 and 15% burnoff. Samples up through 12% burnoff were prepared by reacting in air at 400° C, or below; while those at

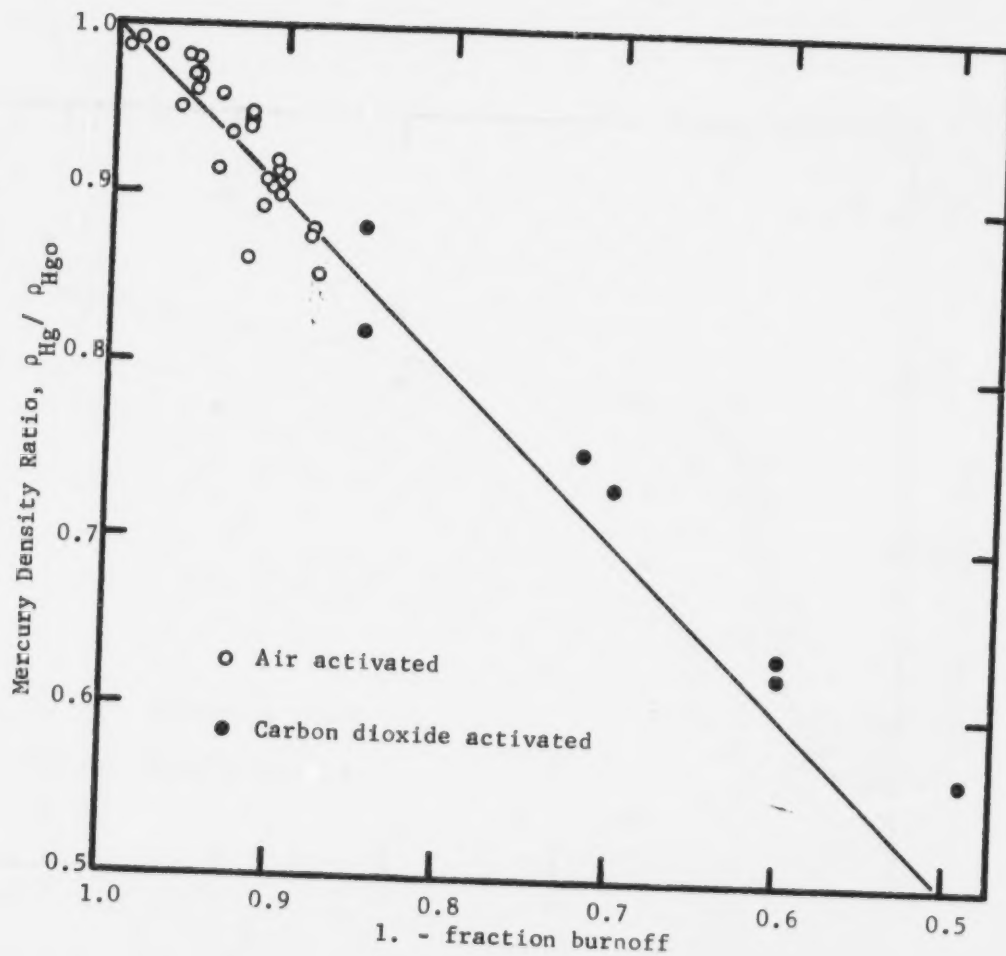


FIGURE 4. RATIO OF SAMPLE-TO-INITIAL MERCURY DENSITY VERSUS BURNOFF

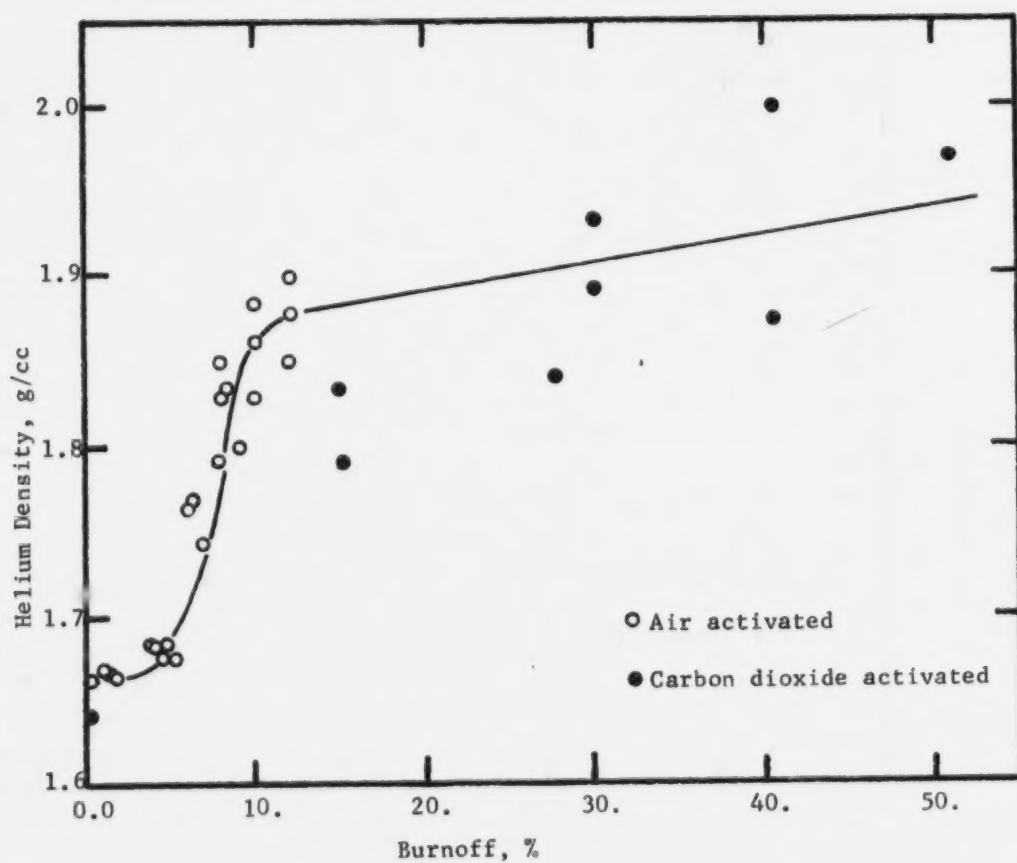


FIGURE 5. HELIUM DENSITY VERSUS BURNOFF

burnoffs of 15% and greater were reacted with carbon dioxide at 800 or 900°C. Thus, the sharp drop in helium density is probably due to the different burning conditions rather than an effect of burnoff alone. Nonetheless, the trend seems consistent. Between 0 and 12% burnoff, there is a distinct correlation between helium density and micropore volume as may be seen by comparing Figure 6 with Figure 5. Above 12% burnoff, this relationship does not appear to hold. This correlation will be considered in the discussion section.

The helium molecule has a diameter of approximately 2.3 Å. Thus helium will penetrate all pores with openings greater than about 2.3 Å wide, and the only spaces helium will not penetrate are the solid itself and "closed" pores (i.e., pores with openings smaller than the helium molecule). The only ways in which the helium density could be increased, then, are: 1) a change in the solid density due to mobility of the solid, recrystallization, or due to selective gasification of fractions with densities lower than that of the remaining solid; or 2) for the solid initially to contain pores impenetrable by helium and for some of these pores to become "opened" (i.e., penetrable by helium).

The first point cannot fully explain the observed helium-density increases. Changes in the solid density seem to be very unlikely because, when the calcinate was heated in an inert gas to typical reaction temperatures, the helium density did not change (even when there was a loss of weight). Further, in order to explain the shape of the helium density vs. burnoff curve, Figure 5, it would be necessary that the solid volatilized up to 5% burnoff have a density of about 1.66 g/cc, that between 5 and 12% burnoff it have a density considerably less than 1.0 g/cc, and that above 12% burnoff it have a density of 1.8 to 2.0 g/cc. There is no basis for postulating such a variation in solid density. It is concluded, therefore, that the observed increases in helium density were a result of the opening of closed pores. This conclusion is consistent with the earlier conclusion that the observed increase in reaction rate at low burnoffs was a result of the exposure of active surface, presumably by opening closed pores.

Total and macropore volumes increased with increased burnoff. Micropore volume increased up to 12% burnoff, but at higher burnoffs, it tended to be about constant or to decrease. The BET surface area showed substantial increases up to 15% burnoff. Above 15% burnoff, surface area increased little.

The results in Table 7 show that the macropore volume of the starting materials ranged from two to ten times greater than the micropore volume. The results also show that at burnoffs of 15% and greater, virtually all of the change in pore volume was in the macropores. At burnoffs below 12%,

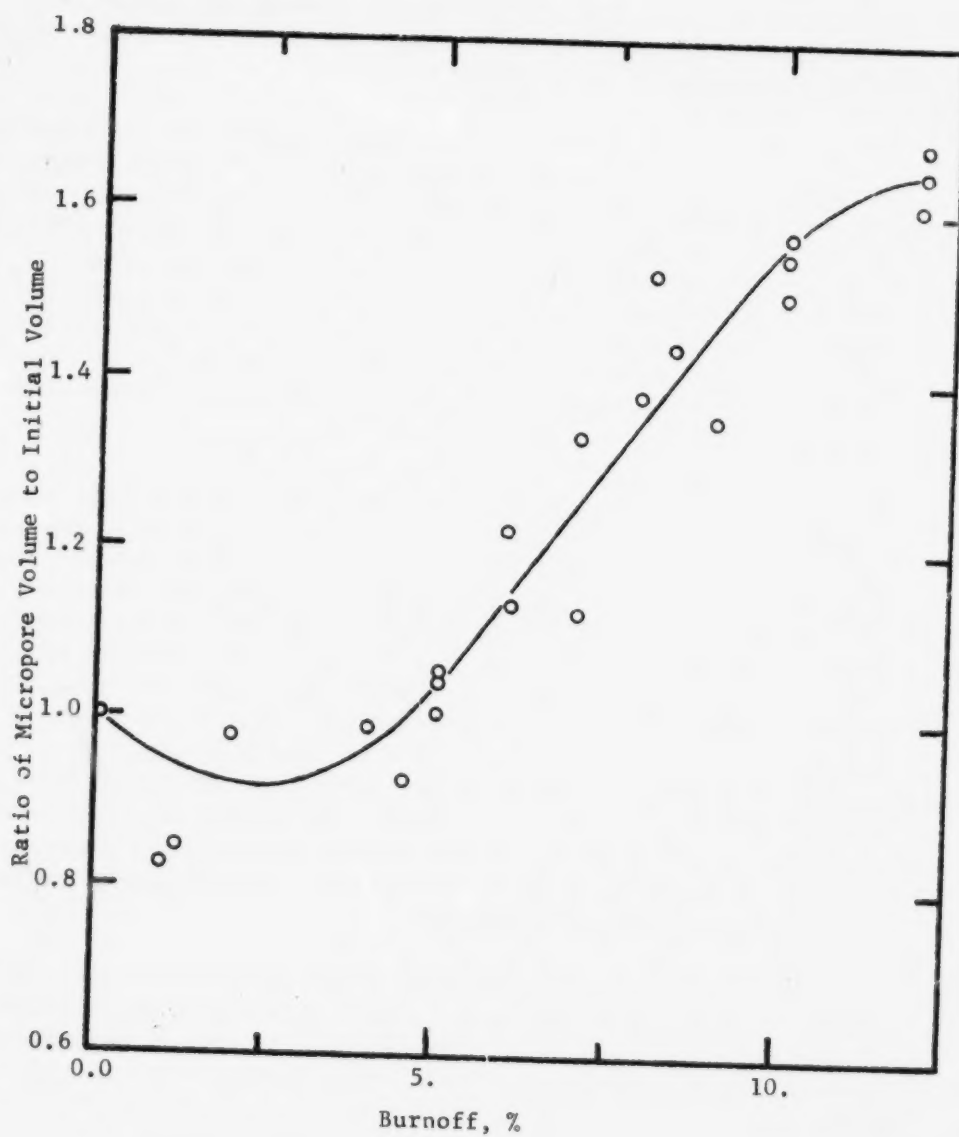


FIGURE 6. MICROPORE-VOLUME RATIO VERSUS BURNOFF

the changes in volumes of the macropore and micropores were comparable. This suggests that burning, at least at higher burnoffs, occurs primarily in macropores. This will be more clearly demonstrated in the discussion section.

Typical cumulative-macropore-volume results are shown in Figure 7. These results show that most of the macropore volume lies in the range with radii between 0.1 and 10 μ and that, as burnoff proceeds, the cumulative volume curves shift to higher radii. In Figure 8, the data of Figure 7 are replotted as normalized cumulative macropore volume, defined as $(\bar{V}_{pM} - \bar{V}_0)/(\bar{V}_T - \bar{V}_0)$, where $\bar{V}_{pM}$ is the cumulative macropore volume at a given radius, $\bar{V}_T$ is the total cumulative macropore volume and $\bar{V}_0$ is the cumulative volume at a radius where the volume curves tend to flatten out at large radius. The normalized curves are somewhat easier to compare and are useful for analysis, as will be shown in the discussion section.

The distribution of volume by radius interval is more apparent when macropore-volume distributions are plotted against radius as shown in Figure 9. The volume distribution, $d\bar{V}_{pM}/d \ln r$, is obtained by differentiating the cumulative volume data with respect to the log of the pore radius, or a normalized distribution may be obtained by differentiating the normalized data. The differentiation may be performed numerically, graphically, or by differentiating an analytical expression for the cumulative volume, as will be presented later. The results shown in Figure 9 are from cumulative volume data differentiated graphically. It is interesting to note that the volume distribution curves appear to have the shape of a normal (gaussian) distribution; that is, normal in the value of the log of the radius. This observation will be made use of in the discussion section. It is clear that as burnoff proceeds, the maximum in the volume distribution shifts to higher radii.

Cumulative-volume data may be used to estimate the surface area of the macropores based on an assumed pore shape. For cylindrical pores, the surface area, dS_i , included in a narrow range of pore radii is given by $dS_i = 2dV_i/r_i$ where dV_i is the pore volume in the radius range and r_i is the mean radius over that range. Summing the dS_i 's (starting at large radius) gives the cumulative surface area in pores larger than any given radius. This has been done for the macropores and micropores, and the results are presented later in Table 9.

Some cumulative micropore volume results are presented in Figure 10. These results are shown as solid curves for radii greater than 10 $\text{\AA}$ and as dashed curves below that radius because of the difficulty in

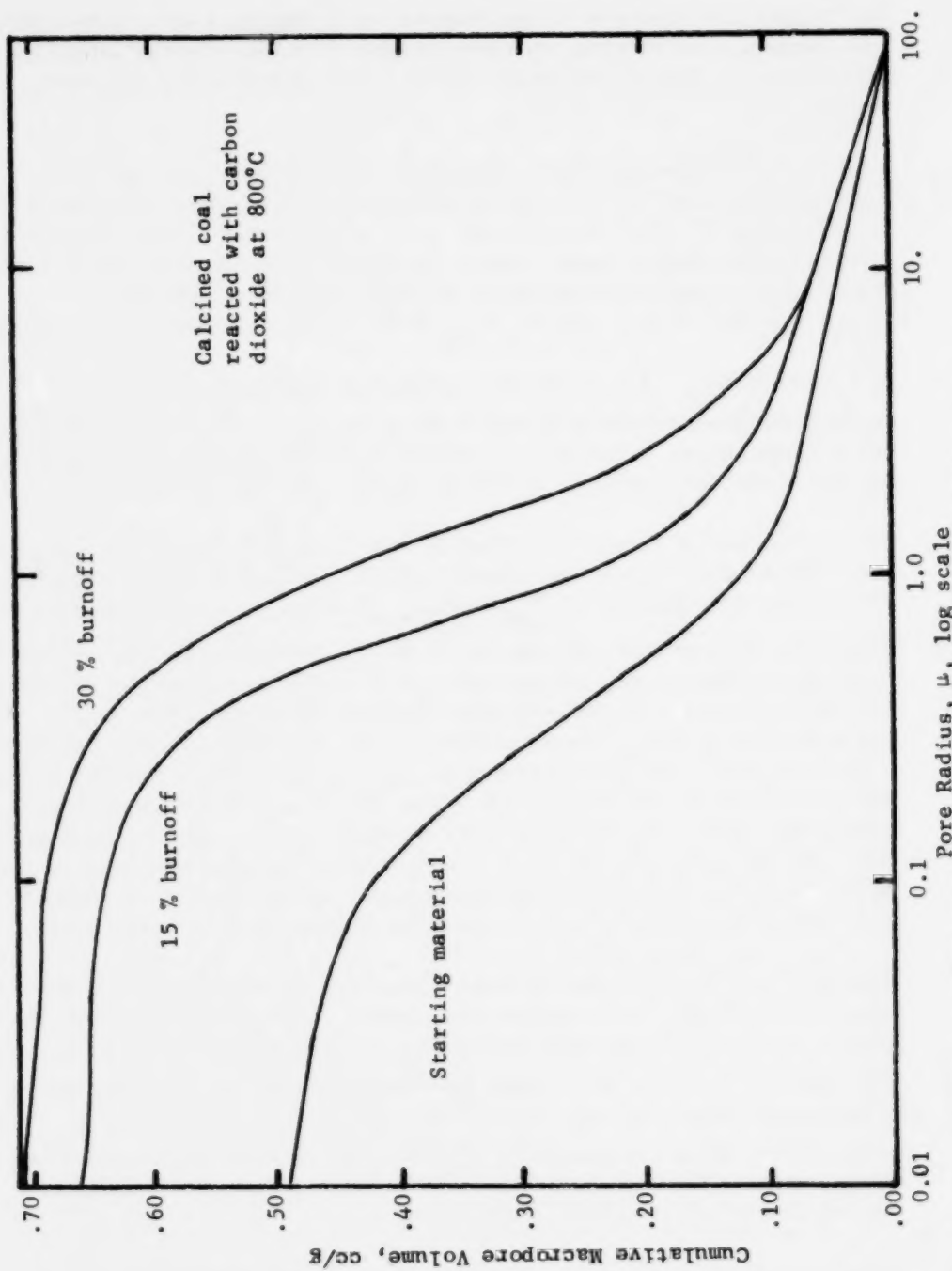


FIGURE 7. CUMULATIVE MACROPORE VOLUME VERSUS RADIUS

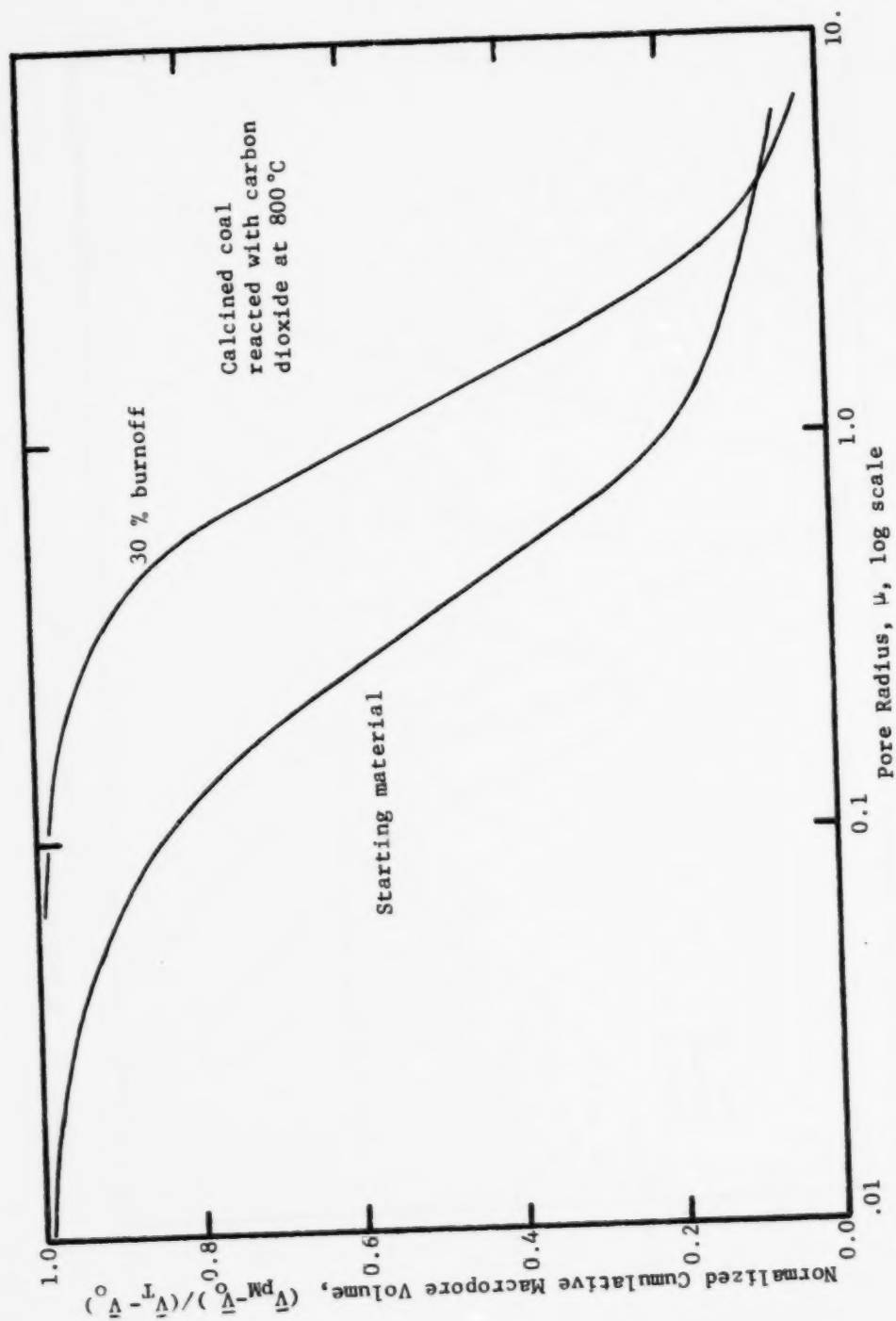


FIGURE 8. NORMALIZED CUMULATIVE MACROPORE VOLUME VERSUS RADIUS

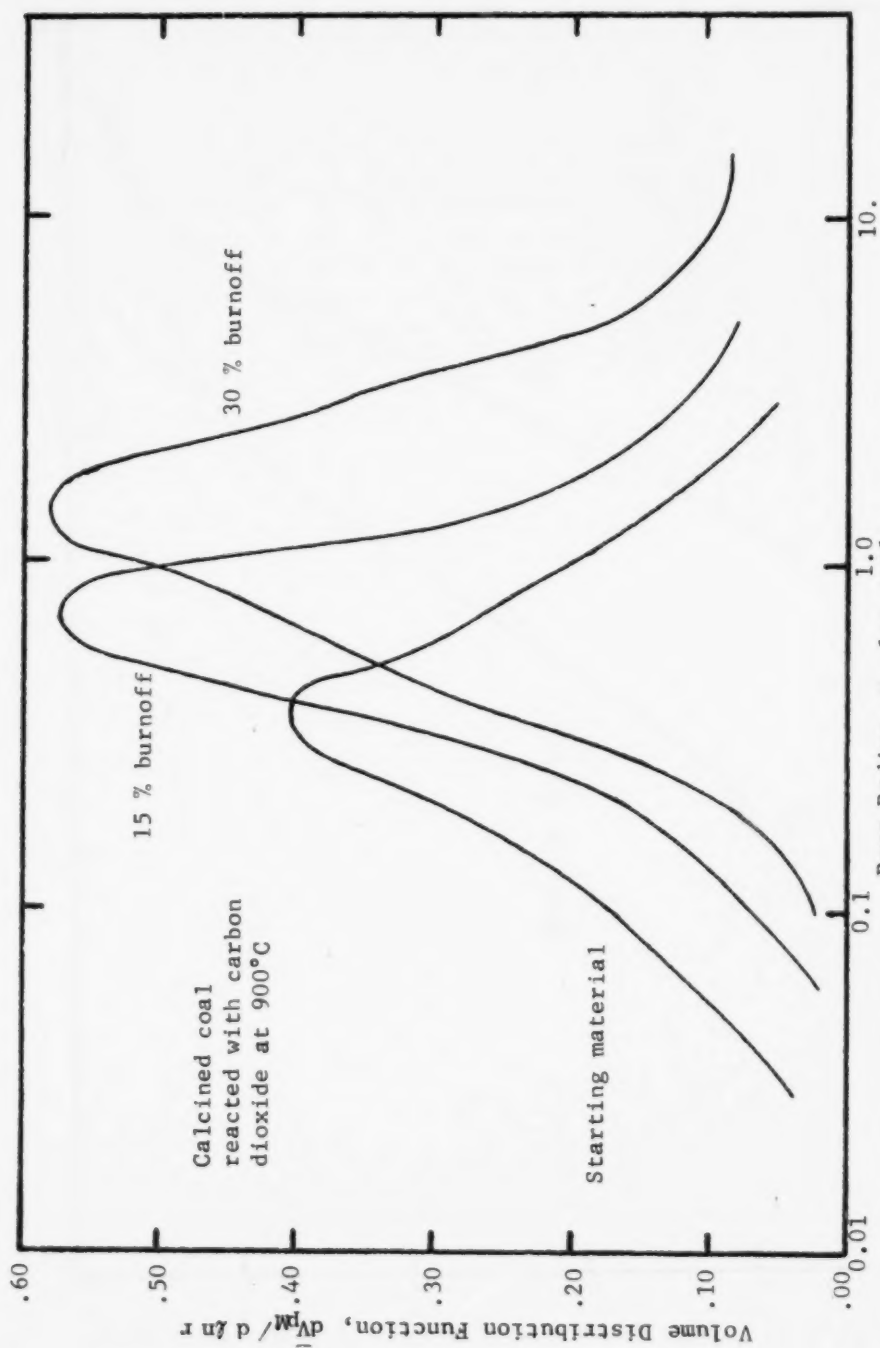


FIGURE 9. MACROPORE-VOLUME DISTRIBUTION VERSUS RADIUS

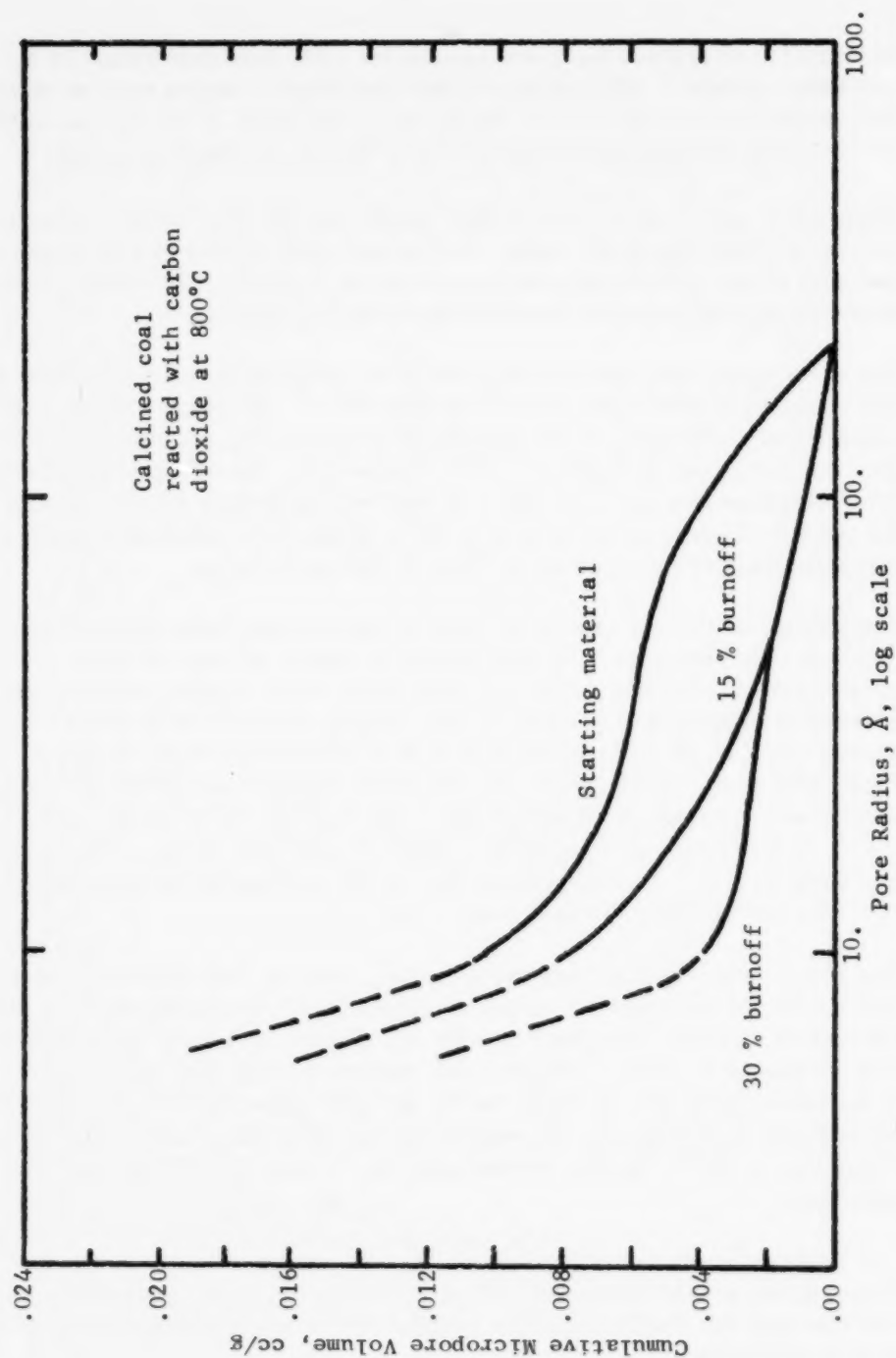


FIGURE 10. CUMULATIVE MICROPORE VOLUME VERSUS RADIUS

interpreting nitrogen-adsorption results for radii less than about $16 \text{ \AA}$, as discussed earlier. Micropore-volume-distribution curves may be obtained from cumulative volume data. These were calculated by numerical differentiation of the cumulative volume data by a digital computer program.

Examples of micropore-volume-distribution results are shown in Figure 11. It is to be noted that in all cases, the volume distribution was increasing at the point where calculations were terminated (Usually $7 \text{ \AA}$ radius), indicating large volumes of very fine micropores in the activated coal.

The presence of very fine micropores in the coal can be shown in other ways. The volumes of pores with radii less than $100 \text{ \AA}$, but large enough to be penetrated by nitrogen, were calculated from the nitrogen-adsorption data (41) and are shown in Table 8. For comparison, the volumes of micropores determined previously from mercury and helium-density measurements and the volume of pores of greater than $10 \text{ \AA}$ radius from cumulative volume measurements are also given in Table 8, when available.

Comparison of the micropore volumes as determined from nitrogen adsorption with those from mercury and helium densities shows the latter to be much greater than the former. This is apparently due to a large pore volume accessible to helium, but not nitrogen, though it may also be due to the assumption that nitrogen in the very fine pores has the same density as bulk-liquid nitrogen. Also, the total micropore volume determined by nitrogen adsorption is two to five times greater than the volume of pores in the 10 to $100 \text{ \AA}$ radius range as determined from nitrogen adsorption. These results are indicative that a substantial portion of the micropore volume consists of very fine pores with radii less than $10 \text{ \AA}$.

The results show another interesting point; that is, that while the total micropore volume tended to decrease slightly with increased burnoff, the micropore volume determined by nitrogen adsorption nearly always increased with increased burnoff. Finally, the results indicate that greater increases in micropore volume, as indicated by nitrogen adsorption, took place with the addition of helium as compared to carbon monoxide, and at 900°C as compared to 800°C in pure carbon dioxide. These results are not fully understood.

For liquid-phase-adsorption carbons, the intermediate-size micropores (i.e., those greater than about $10 \text{ \AA}$ radius) are probably far more important than are the fine micropores included in the volume determined by helium penetration.

Surface-area results are also of interest; these are shown in Table 9.

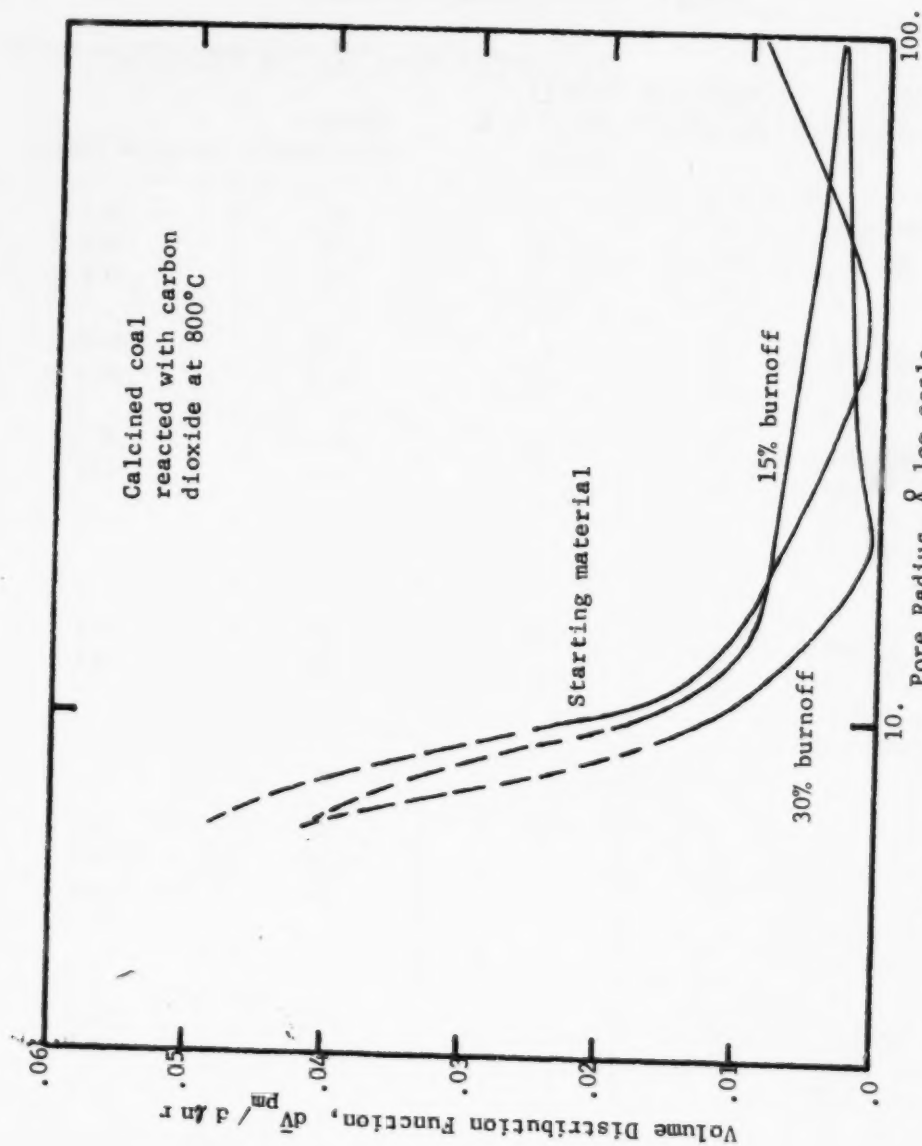


FIGURE 11. MICROPORE-VOLUME DISTRIBUTION VERSUS RADIUS

Table 8 - MICROPORE VOLUMES

SAMPLE PREPARATION	PERCENT BURNOFF	MICROPORE VOLUME, cc/g of starting material		
		TOTAL, Mercury & Helium	Nitrogen Adsorption	> 10 Å radius
Carbon Dioxide, 800° C	0 ¹	.11	.023	.010
	15	.09	.028	.008
	30	.07	.021	.004
Carbon Dioxide, 900° C	15	.10	.026	.008
	30	.11	.033	.012
Carbon Dioxide, 15% burn-off at 800° C, remainder at 900° C	27.8	.08	.035	.014
	40.5	.07	.046	.023
Carbon Dioxide, 30% burn-off at 800° C, remainder at 900° C	40.5	.07	.037	.014
	51	.07	.038	.015
80% carbon dioxide, 20% carbon monoxide, 888° C	0 ²	-	.027	.008
	15	-	.025	.007
	30	-	.023	.006
80% carbon dioxide, 20% helium, 872° C	15	-	.032	.012
	30	-	.028	.010

1. Starting material was calcined coal heated in nitrogen for 1½ hrs at 1300° C.

2. Starting material was calcined coal heated in nitrogen for 16 hrs at 1100° C.

Table 9 - SURFACE AREAS

SAMPLE PRE- PARATION	PERCENT BURNOFF	SURFACE AREA, m ² /g of starting material			
		BET	Macropore, cumulative	Micropore, cumulative ³	Total, cumu- lative
	0 ¹	28.	5.4	7.4	12.8
100% Helium, 880°C.	0	33.	--	--	--
80% CO ₂ , 20% CO, 872°C	15	45.	3.4	6.3	9.7
	30	46.	3.0	6.8	9.8
80% CO ₂ , 20% He, 888°C	15	47.	3.0	12.7	15.7
	30	48.	3.0	9.8	12.8
	0 ²	38.	4.6	7.2	11.8
CO ₂ , 800°C	15	46.	2.7	8.7	11.4
	30	43.	1.9	4.3	6.2
CO ₂ , 900°C	15	52.	2.6	9.0	11.6
	30	60.	2.2	15.1	17.3

1. Starting material was calcined coal heated in nitrogen for 16 hrs at 1100°C.
2. Starting material was calcined coal heated in nitrogen for 1½ hrs at 1300°C.
3. Cumulative micropore area calculated for pores larger than 10 Å radius and less than 100 Å radius.

The results in Table 9 show very large differences between the BET surface area and the cumulative surface area of pores with radii between 10 and 100 Å. The differences here are greater than those usually observed, but such differences are not unusual when pores with radii less than 14 Å are present (12, 53). The differences are apparently due to the presence of the small micropores, plus also probably the assumption of cylindrical pores.

The results for micropore-volume changes upon activation give a picture which is difficult to analyze. There is relatively little increase in total micropore volume; indeed, there is a tendency for total micropore volume to

decrease at burnoffs higher than 15%. There are, on the other hand, increases in the volume of micropores accessible to nitrogen and increases in BET surface area. In contrast, there was substantial growth in helium-penetrable-micropore volume in calcined coal activated with air at up to 400°C and burnoffs up to 12%. Micropore growth will be considered further in the discussion section.

Graphite Activation

The reaction of graphite with carbon dioxide gave interesting results about pore growth which have been published (54).

The results are summarized in Table 10. As was pointed out earlier, diffusion was partially rate limiting in the large graphite cylinders. The data presented in Table 10 are the ratio of the pore volume in a certain pore radius increment of a reacted sample to the pore volume in that same increment in the unburned sample, considering only the outer radial one-third of the cylinder (as obtained by grinding off the inner two-thirds). Similar results were obtained in the middle and inner thirds, but the development of pore volume was somewhat slower as the center of the cylinder was approached, due to diffusion limitations.

Table 10 - RELATIVE INCREASES OF PORE VOLUME
IN GRAPHITE DUE TO ACTIVATION

% BURNOFF	RATIO OF PORE VOLUME IN REACTED SAMPLE TO INITIAL PORE VOLUME IN PORE RADIUS INTERVALS SHOWN			
	0	10	20	30
RADIUS INTERVAL, Å				
70-200	1	1	2	3
200-500	1	3	2	2
500-1,000	1	7	8	9
1,000-3,000	1	8	10	10
3,000-6,000	1	3	4	4
6,000-10,000	1	1	2	2
10,000-20,000	1	2	2	2
20,000-50,000	1	1.2	1.2	1.7
> 50,000	1	2	2	6

The graphite burning results show that during the first 20% burnoff, the most rapid pore growth was in the 500 to 3,000 Å pore-radius range. Above about 20% burnoff, little or no additional growth occurred in that size range, but rather the larger pores, especially those of radii greater than 20,000 Å (2μ), grew relatively more. This is especially noteworthy when it is recognized that in the unburned graphite, more than half of the total pore volume was in the 20,000 to 50,000 Å radius range. Similar observations (i.e., the relatively more rapid growth of smaller pores) were made earlier by Walker et al. (48) and by Dubinin et al. (24, 55) - in the former case for sizes similar to those in the present study, and in the later case for much smaller pores, ca. 6.8 Å.

These observations are explained as follows (54). Graphitized carbon contains large crystallites, typically of the order of 1000 Å thick in the direction normal to the basal plane (56). Graphite crystallites are known to be much more reactive in the direction parallel to the basal plane than in the direction normal to the basal plane (57). Thus graphite crystallites would tend to burn parallel to the basal plane, producing pores with dimensions comparable to the thickness of the original crystallite. This is apparent in the pore volume increases in the 500 to 3000 Å range in Table 10. This type of burning would occur preferentially as long as crystallites of the proper size were available and had faces normal to the basal plane exposed to the reacting gas. Growth of these pores would terminate abruptly when the supply of such crystallites was exhausted. Again, rapid termination of growth in the 500 to 3000 Å pore-size range occurred. Only when the crystallites were gone did burning of carbon from the surface of other pores become the predominant mechanism. This is shown by the results in Table 10 where large-pore growth predominates between 20 and 30% burnoff. Indeed up to 20% burnoff, only about 20% of the total pore-volume increase was in the 20,000 to 50,000 Å pore-size range; while from 20 to 30% burnoff, about 70% of the total burnoff occurred in that size range.

Thus, pore growth in graphitized carbon can be rather well explained. The mechanism suggests a way of producing pores of a desired size in an activated carbon: that is, start with a material containing a high concentration of graphite crystallites of the size of the desired pores.

SECTION VI

DISCUSSION

The results presented in section V indicate that in the reaction of a calcined coal with air or carbon dioxide, carbon removal occurs primarily in the macropores. The reaction rate is chemical rate controlled, not diffusion controlled, in the macropores. There is micropore growth under some conditions. Micropore growth is associated with changes in helium density and is, at least partially, diffusion limited.

In graphite, pore growth was shown to occur largely by end-burning of graphite crystallites. Graphitic crystallites in the calcined coal are probably about 6 Å in thickness (21). If these reacted by end-burning, they would lead to micropores.

In this section, the changes in pore volume will be examined and compared with pore burning models in an effort to describe the pore-volume changes which occur upon activation. The results of this study will be compared with other recent investigations of activation and reactivation.

Total Pore Volume

The total pore volume in calcined coal was found to increase with increased burnoff of carbon. Increased burnoff was accompanied by increases in helium density which were ascribed to the opening of pore volume initially present but inaccessible to helium. It was shown, based on the change in mercury density, that substantially all of the burning occurred internal to the particles and that thus the size of the particles did not change significantly during burning.

The measured total pore volume of a sample was determined by inserting experimentally measured values of the mercury and helium densities into equation 1. If the new pore volume resulting from activation was only the void volume equal to the volume of carbonaceous material removed by reaction, the total pore volume in a sample would equal the initial pore volume plus the mass divided by the density of the material removed by reaction. The density of the removed material is not known nor is it measurable. In order to estimate the new pore volume created, it was assumed that the reacted solid had the same density as the remaining solid. A value of 2.0 g/cc was assumed for the density of the non-porous solid, because that was the highest helium density measured on any of the activated samples in this work and because it was the value approached by all samples at high percentage burnoffs. Thus, 2.0 g/cc seemed to be a good approximation of the true solid density.

Total pore volumes calculated in the preceding manner will be called those "calculated due to burnoff". When these volumes were compared with measured total pore volumes, it was found that the measured values were greater than the calculated values in twenty-five of the thirty cases for which measured total pore volume values were available (the data used were from Tables 7 and 7a with burnoffs referred to unburned calcinate). Four of the five exceptions were at burnoffs of 5% or less, where both the measured and calculated volume changes were very small; the fifth exception was at 51% burnoff where it is likely that there was some external burning. Thus the evidence is strongly indicative that the total pore volume increased by more than would be predicted based on the volume of material removed.

A model for total pore-volume development during burning was derived from the foregoing observations by assuming: 1) all carbon removal was internal, and particle size did not change and, 2) that the change in helium density was due to opening of closed pores. The development of the model is given in Appendix 1. The model gives the total pore volume, in cc/g of starting material, after any fraction burnoff, f , by the equation,

$$\bar{V}_p = \frac{1}{\rho_{Hgo}} - \frac{(1-f)}{\rho_{He}} \quad (5)$$

That is, the total pore volume should be predictable from the initial mercury density, the fraction burnoff and the sample helium density. Values of the total pore volume in a sample calculated from equation 5 will be called those "calculated by model".

Figure 12 shows representative values of the total pore volume as measured, as calculated due to burnoff, and as calculated by model. The values are plotted as the ratio of the total pore volume of a sample at a certain burnoff to the initial total pore volume of that sample (at zero burnoff). This ratio was used because the samples had different initial total pore volumes. Figure 12 shows that through 15% burnoff the measured and calculated-by-model total pore volumes agree very well; also that at 30 and 40% burnoff the measured values fall below the calculated-by-model values but fall above the values calculated due to burnoff alone. At 51% burnoff the measured total pore volume was less than that calculated by either method. As indicated earlier, it is likely that external burning occurred in that sample.

The results shown in Figure 12 lend strong support to the assumptions of the model. In particular, they tend to confirm the idea that the change in helium density is due to the opening of closed pores and that these opened pores contribute to the measurable total pore volume. The rather good correlation between measured and calculated-by-model total pore volumes suggests that there is not much total pore-volume change due to heating alone, even at the higher temperatures, in a predominantly carbon dioxide atmosphere.

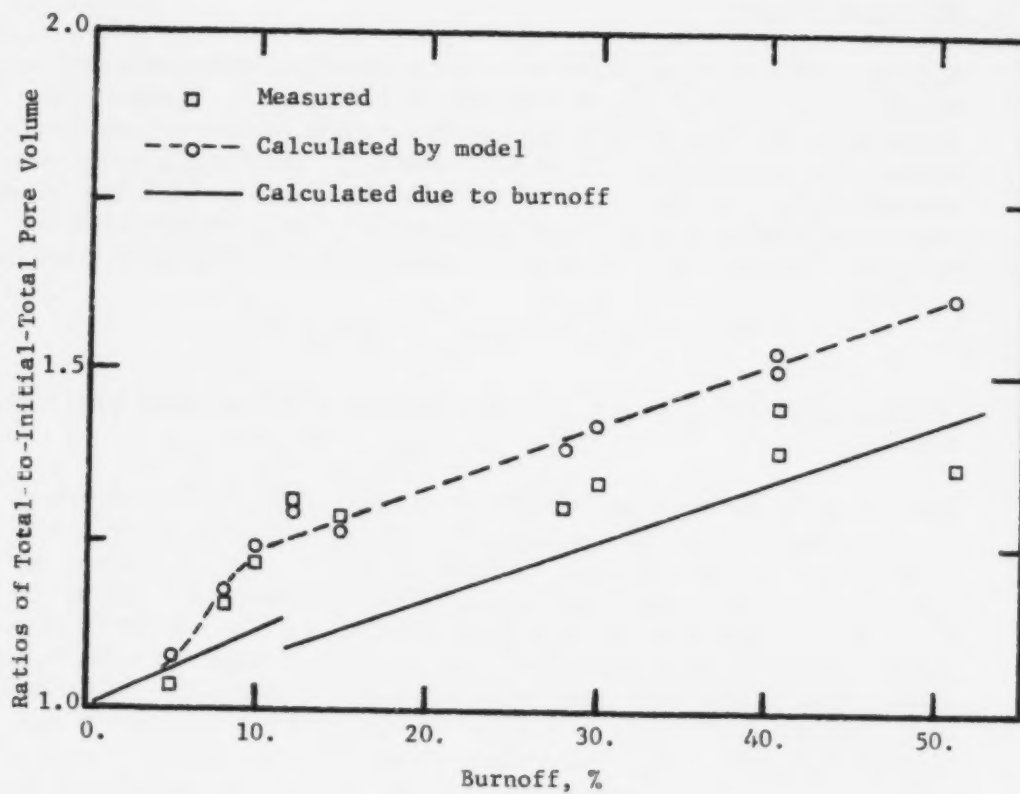


FIGURE 12. MEASURED AND CALCULATED RATIOS OF TOTAL PORE VOLUME VERSUS BURNOFF

However, thermal pore-volume changes as well as particle-size changes may account for those differences that do occur between the measured and the calculated-by-model total pore volumes.

Micropore Volume

Figures 5 and 6 show that there is a close correlation between micropore volume and helium density, at least through 12% burnoff. Based on this observation, it was postulated that the closed pores that were opened by burning were micropores. To test this postulate, the burning model was extended to attribute micropore-volume changes only to the opening of closed pores. This development, shown in Appendix 1, gave the result that the micropore volume, $\bar{V}_{pm}$, in cc/g of starting material, should be given by

$$\bar{V}_{pm} = \bar{V}_{pmo} + 1/\rho_{Heo} - (1-f)/\rho_{He} - f/\rho_C \quad (6)$$

A "calculated micropore volume" at each burnoff was determined from equation 6.

The calculated and measured micropore volumes up to 12% burnoff are shown in Figure 13 (measured micropore volume refers to measured total pore volume, minus measured macropore volume). It is to be observed that there is excellent qualitative and quantitative agreement. There is a slight effect of temperature, with higher temperatures giving higher measured volumes but giving about the same calculated volumes as lower temperature. This temperature effect is unexplained. Nonetheless, this result shows that micropore-volume changes, at temperatures up to 400°C and burnoffs up to 12%, were essentially due entirely to the opening of closed pores. At higher temperatures and burnoffs, this correlation did not occur.

Thus, it has been shown that pore-volume changes occur by three mechanisms: the first is due to heating only, which seems not to be important under activation conditions; the second is due to the void space left by the removal of carbon; and the third is a result of burning making accessible closed pores that were already present in the starting material. Both burning and opening of closed pores were shown to contribute to total pore volume when the burning took place in carbon dioxide at 800°C, and above. Total micropore volumes calculated from equation 6 are compared with measured total micropore volumes in Table 11. It is quite clear from the results in Table 11 that the measured and calculated total micropore volumes do not agree for carbon dioxide activation. Indeed, though the calculated micropore volumes increased with burnoff, the measured volumes tended to decrease slightly.

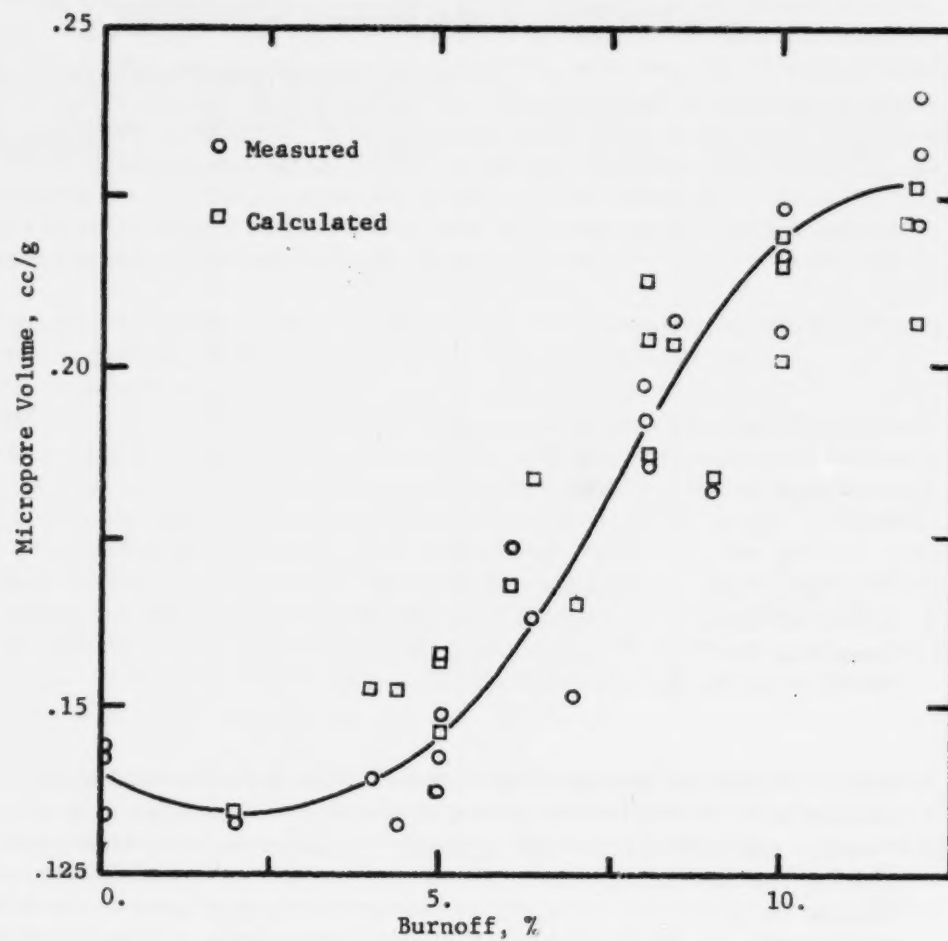


FIGURE 13. MEASURED AND CALCULATED MICROPORE VOLUMES VERSUS BURNOFF

Table 11 - CALCULATED AND MEASURED TOTAL MICROPORE VOLUMES FOR CARBON DIOXIDE ACTIVATION

SAMPLE PREPARATION	PERCENT BURNOFF	TOTAL MICROPORE VOLUME, cc/g of starting material	
		Measured	Calculated
Carbon dioxide, 800° C	0	.11	--
	15	.09	.17
	30	.07	.21
CO ₂ , 900° C	15	.10	.18
	30	.11	.20
CO ₂ ; 15% burn-off at 800° C, remainder at 900° C	27.8	.09	.19
	40.5	.08	.22
CO ₂ ; 30% burn-off at 800° C, remainder at 900° C	40.5	.09	.20
	51	.10	.22

There are several possible explanations for the differences in micropore results from carbon dioxide activation as compared to those from air activation. One is that up to 12% burnoff, opened pores were micropores; but with increased burning, these micropores burned and were enlarged to become macropores. A second is that as macropores grew by burning, they grew to include or engulf the existing micropores. A third is that in carbon dioxide, the opened pores were macropores. None of these explanations is entirely satisfactory.

It is difficult to conceive that quite suddenly, between 12 and 15% burnoff, the micropores burned to become macropores or that macropores engulfed micropores. Further, none of the micropore cumulative volume curves showed significant volume increases in pores greater than about 50 Å radius, suggesting that in no case was there sufficient growth of micropores to become macropores. On the other hand, it is difficult to conceive that pores that were opened as micropores by air were macropores when opened by carbon dioxide. It should be remembered, though, that heating alone to temperatures similar to those necessary for carbon dioxide activation did cause pore-volume changes, notably increases in macropore volume and decreases in micropore volume. Still another observation worth considering

was that, whereas the reaction rate with carbon dioxide increased during the first 10% burnoff (this is ascribed to the exposure of additional reactive sites), the reaction rate remained constant throughout the first 12% burnoff with air. This suggests that the opened pores were reactive to carbon dioxide but not to oxygen; this is consistent with the growth of micropores upon carbon dioxide activation. It is unfortunate that there is not more overlap of the data for the two activating gases. From the available data it is only possible to observe that the development of micropore volume was quite different in the cases of oxygen and carbon dioxide as the activating gases; it is not possible to determine why they are different.

The results in Tables 7 and 9 show that the BET surface area increased with burnoff. Indeed, from Tables 8 and 9 it can be seen that there is a correlation between the volume of micropores accessible to nitrogen and the BET surface area, as would be expected since both values are obtained from nitrogen isotherm data. This correlation is further emphasized in Table 12 and in Figure 14. The plot in Figure 14 shows that surface area is related to the corresponding volume by a straight line through the origin. Although there is considerable scatter, the trend is very distinct. The inverse of the slope of Figure 14 is related to the average pore radius. Assuming cylindrical pores, an average micropore radius of about 6 Å is obtained. Table 12 shows that the volume of micropores, less than 10 Å radius and accessible to nitrogen, increases considerably in the first 15% burnoff and is relatively constant at greater burnoffs.

In the Results section it was pointed out that during carbon dioxide activation, the rate of reaction in the micropores was partially diffusion limited. There are not sufficient kinetic data to determine whether diffusion was rate limiting in air activation. However, since the reaction rates were comparable and the diffusivities were lower at lower temperature, it seems probable that diffusion was at least partially rate limiting in the pores during air activation. Nonetheless, partial diffusion control hardly seems an adequate explanation for the fact that essentially all burning occurred in the macropores. The surface area in the micropores was always greater than that in the macropores, frequently by a factor of ten. Thus, if the chemical reaction rate per unit surface area was independent of pore size, then even if diffusion reduced the rate by 50%, it would be expected that considerable reaction would still occur in the micropores. That this did not occur is strong, indirect evidence that the surface is not uniformly reactive, but rather that the surface in the macropores is more highly reactive than that in the micropores. A possible explanation for this is that active sites, for example catalytic sites, are not uniformly distributed. That such is the case seems quite possible, but there is no known direct evidence that it is true.

Table 12 - MICROPORE VOLUME AND SURFACE AREA

SAMPLE PREPARATION	PERCENT BURNOFF	SURFACE AREA, m ² /g of starting material			PORE VOLUME, cc/g of starting material	
		BET	PORES < 100 Å	PORES < 10 Å, by nitrogen	PORES < 100 Å	PORES < 10 Å, by nitrogen
Starting material	0	38	34	26	.023	.013
Carbon dioxide, 800°C	15	46	43	35	.028	.020
	30	43	41	37	.021	.017
CO ₂ , 900°C	15	52	49	40	.026	.018
	30	59	57	41	.033	.021
CO ₂ ; 15% burn-off at 800°C, remainder at 900°C	27.8	60	57	42	.035	.021
	40.5	72	69	41	.046	.023
CO ₂ ; 30% burn-off at 800°C, remainder at 900°C	40.5	64	62	41	.037	.023
	51	67	65	42	.038	.023
Starting material	0	28	22	15	.022	.009
80% CO ₂ , 20% CO, 883°C	15	45	42	35	.025	.016
	30	46	43	36	.023	.016
80% CO ₂ , 20% He, 872°C	15	47	44	31	.032	.017
	30	48	45	36	.028	.015

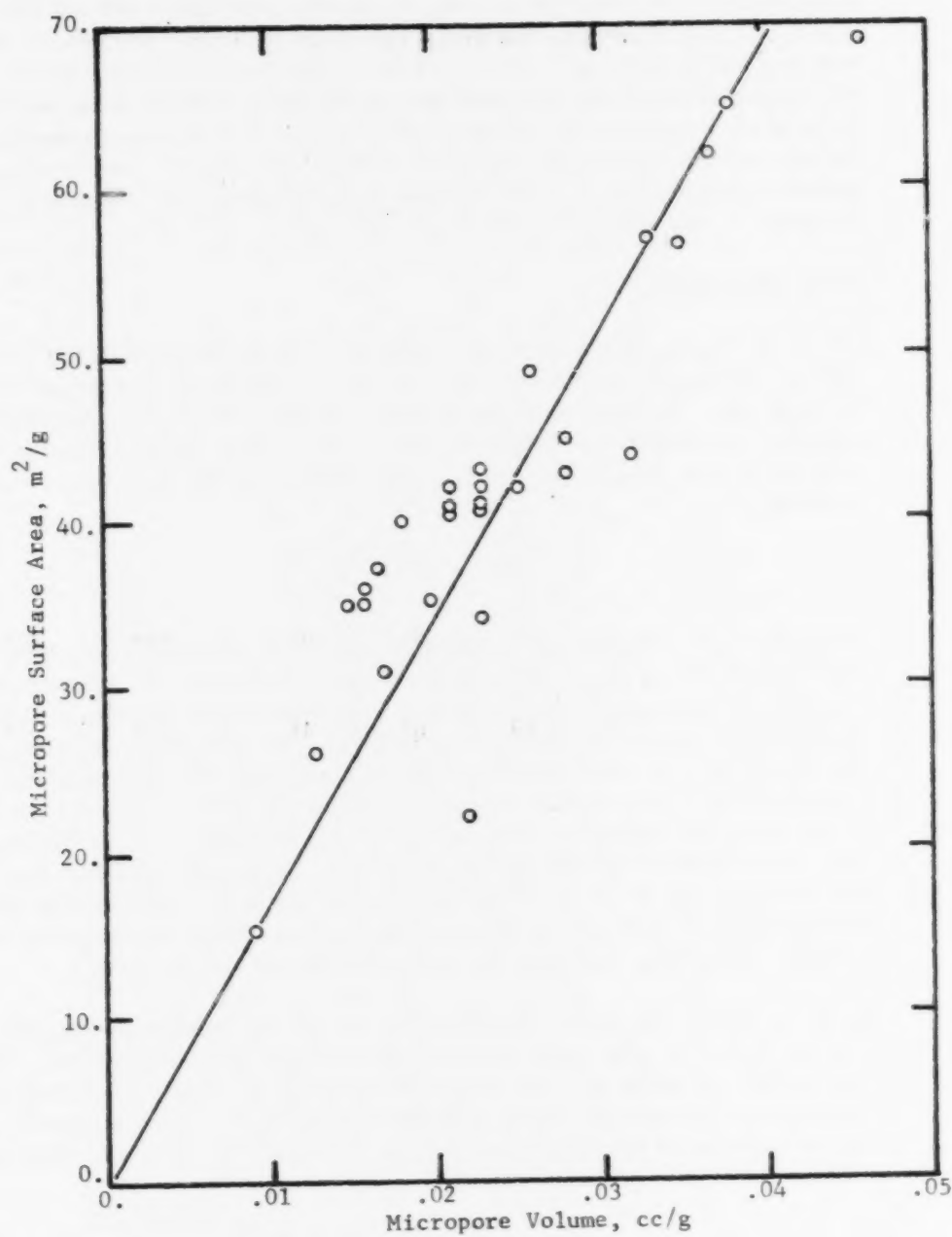


FIGURE 14. MICROPORE SURFACE AREA AS A FUNCTION OF MICROPORE VOLUME

In summary, the observed micropore-growth phenomena are not fully understood. It can be stated, however, that little or no new micropore volume was created by burning. Increases in accessible micropore volume upon air activation were due to closed pores originally present in the carbon that were made accessible by burning. Total micropore volume accessible to helium tended to decrease upon carbon dioxide activation, while nitrogen surface area increased. The surface area increases corresponded to increases in pore volume accessible to nitrogen.

Macropore Volume

As shown above, the opening of closed pores accounted for all the micropore-volume change upon air activation, so the burning must have produced only macropores. The pore-burning model was extended by assuming that all burning occurred in macropores and that macropore-volume changes were due to burning only (see Appendix 1). This yielded for the macropore volume the equation,

$$\bar{V}_{pM} = \bar{V}_{pMo} + \frac{f}{\rho_C} \quad (7)$$

Equation 7 gives calculated macropore volumes. The carbon density, ρ_C , was taken at 2.0 g/cc. Calculated macropore volumes are compared with macropore volumes measured by mercury penetration, each plotted against burnoff in Figure 15 for burnoffs up to 12%. The measured values scatter, but follow the calculated trend and the scatter about the calculated line is quite random. The scatter is emphasized by the scale, but is of the order of the calculated change. The scatter (5.8% average absolute deviation from line) may reflect reproducibility of the data. It is concluded that for burning the calcined coal in air up to 400°C and 12% burnoff, substantially all of the burning occurs in the macropores, that existing closed pores are opened as a result of burning, and that the opened pores are micropores.

Since opened pores did not contribute to micropore volume during carbon dioxide reaction, they must have contributed to macropore volume. That this in fact did occur may be seen by comparing the values of measured macropore volume with values that were calculated by attributing both burning and opening of pores to macropores, as shown in Table 13. The calculated values are from the equation (see Appendix 1),

$$\bar{V}_{pM} = \bar{V}_{pMo} + \frac{1}{\rho_{Heo}} - \frac{(1-f)}{\rho_{He}} \quad (8)$$

The results in Table 13 show that the calculated and measured macropore volumes agree quite well, except at 51% burnoff where external burnoff seems to have been important. These results thus demonstrate that upon

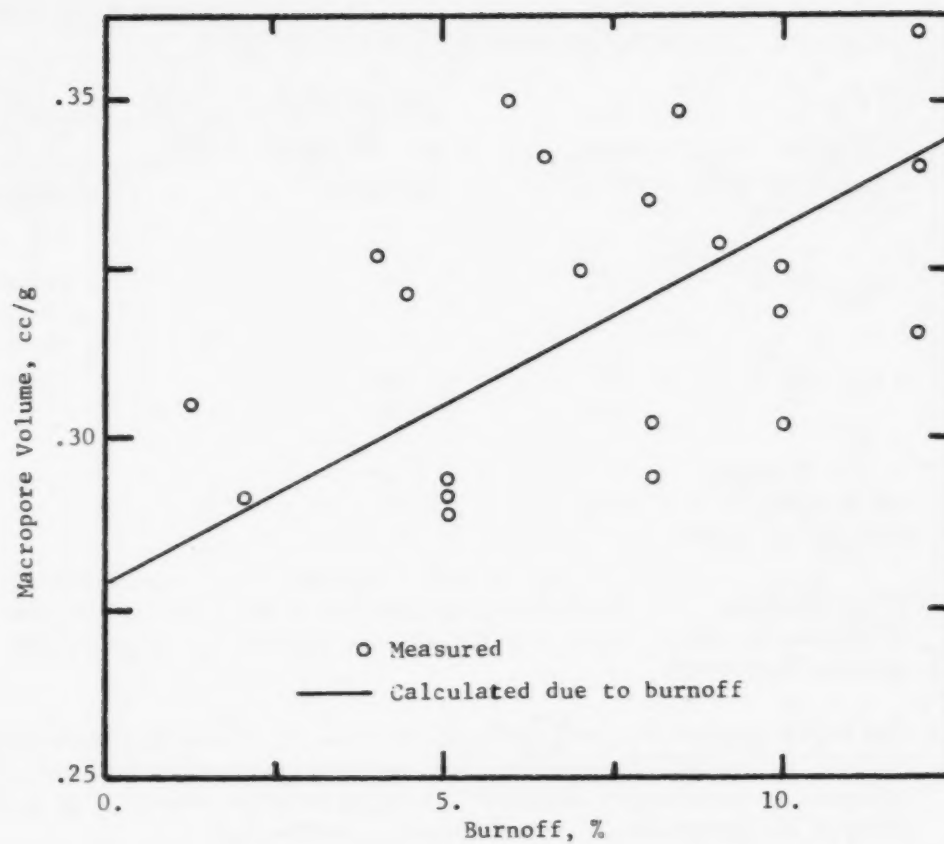


FIGURE 15. MEASURED AND CALCULATED MACROPORE VOLUMES VERSUS BURNOFF

carbon dioxide activation, essentially all the pore volume created by burning and by opening of closed pores contributed to macropore volume.

Table 13 - MEASURED AND CALCULATED MACROPORE VOLUMES
FOR CARBON DIOXIDE ACTIVATION

SAMPLE PREPARATION	PERCENT BURNOFF	MACROPORE VOLUME, cc/g of starting material	
		Measured	Calculated
CO ₂ , 800° C	0	.47	--
	15	.66	.60
	30	.70	.72
CO ₂ , 900° C	15	.58	.61
	30	.65	.71
CO ₂ ; 15% burn- off at 800° C, re- mainder at 900° C	27.8	.67	.69
	40.5	.77	.78
CO ₂ ; 30% burn- off at 800° C, re- mainder at 900° C	40.5	.74	.76
	51	.72	.83

Macropore growth is thus rather well understood, resulting almost exclusively from burnoff of carbon at lower burnoffs and from burnoff and opening of closed pores at higher burnoffs. It might be anticipated that the development of the macropore structure should be predictable.

It was shown earlier that in carbon dioxide activation, the reaction rate in the macropores was chemical reaction controlled, not diffusion controlled. This is also almost certainly the case in air oxidation since the rates are comparable, although this was not explicitly established. One implication of chemical reaction control is that the gas composition throughout the macropore structure was uniform. If it is further assumed that the reactivity of the surface was the same in all macropores, regardless of pore size, then it would be expected that the chemical reaction rate per unit surface area would be the same in all macropores. With this as the basic assumption, a model was developed to predict the macropore-size distribution resulting from burning some fraction of the carbon with a given initial pore-size distribution. The development of the model is shown in Appendix 2. A computer program was written to do the calculations.

For computational convenience, use was made of the fact that the macropore-size distributions were observed to resemble log-normal distributions. A method was developed for fitting the macropore-volume distributions with a log-normal-distribution function. The development of this method is described in Appendix 3. The use of this empirical pore-size-distribution function was not necessary to implement the macropore growth model, but it made programming the computations much easier.

An example of the results predicted by the macropore burning model, compared with the measured pore volume, is shown in Figure 16 in the form of normalized cumulative volume curves. The results shown in Figure 16 are typical; that is, the model did not predict the observed results. Indeed, it did not even come close to predicting them. This was true for the air-activated samples as well as for the carbon-dioxide activated samples. Figure 17 perhaps demonstrates even more clearly the differences by showing the predicted and observed normalized volume distributions. It can be seen that the actual burning caused the smaller radius pores to grow larger much more rapidly than the model predicted, resulting in a shift of the distribution's maximum to much higher values than predicted by the model.

This comparison clearly demonstrates that the assumptions of the macropore-burning model are not correct. The assumption most likely to cause the discrepancies seen is that of uniform surface burning. Thus, the results strongly indicate that the reaction rate per unit surface area is not the same in all pores. It is possible that the assumption of cylindrical pores introduces error, but the model is not especially sensitive to the assumed geometry. Opening of the mouths of ink-bottle pores might account for the observed shifts in pore-size distribution. It has been suggested that gas activation results in reaction primarily at the pore mouth, presumably due to the presence of catalytic sites there (21, 22).

When the foregoing theoretically-based model was found to fail, several strictly empirical models were devised to attempt to correlate the results. Some of these were slight improvements, in particular one in which it was assumed that the volume change of pores in a given size range was proportional to the initial volume of pores in that range; but none adequately fitted the data (41).

The results indicate that even in macropores under chemical-reaction-controlled conditions, the rate of reaction per unit surface area was not uniform. It has already been noted that the surface in the micropores must be much less reactive than that in the macropores. There is thus considerable evidence that the reactive sites are not uniformly distributed in pores of different sizes. It would seem that the nature and distribution of the reactive sites in carbon are the keys to the development of the carbon's pore structure upon activation.

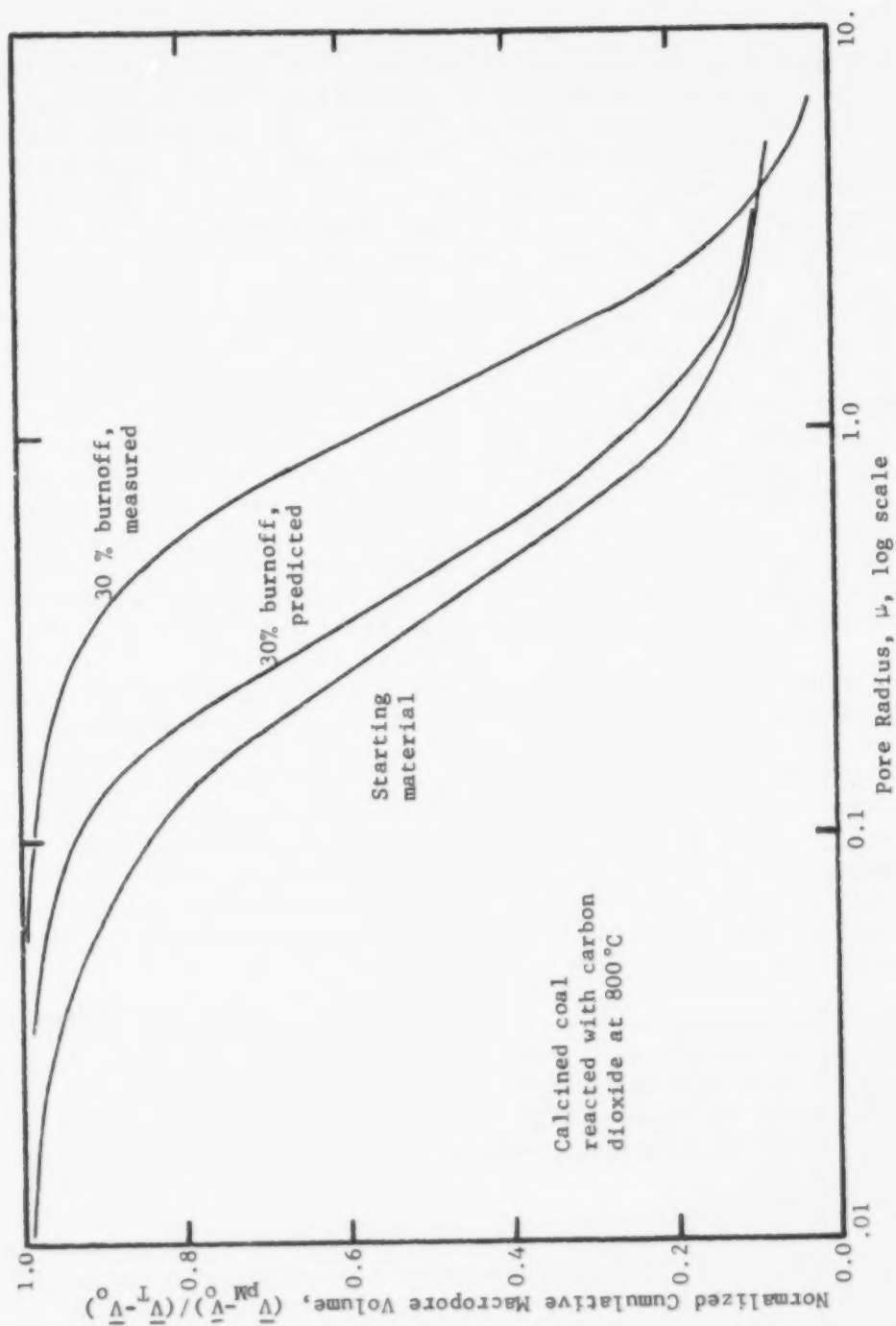


FIGURE 16. PREDICTED AND MEASURED NORMALIZED MACROPORE VOLUMES VERSUS RADIUS

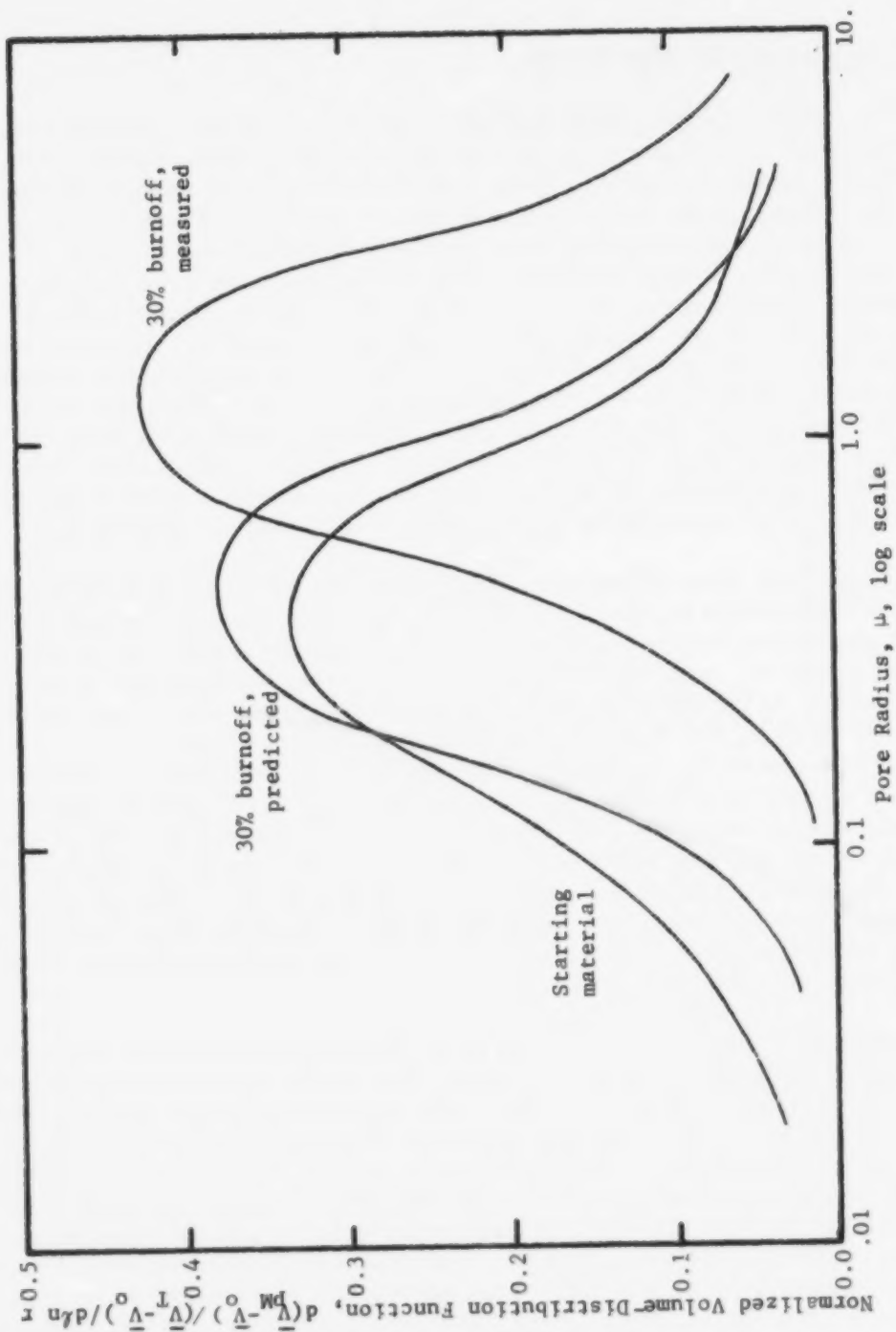


FIGURE 17. PREDICTED AND MEASURED, NORMALIZED, MACROPORE-VOLUME DISTRIBUTIONS VERSUS RADIUS

Comparison with Other Results

The results of some studies similar to the present one have recently been published. Turkdogan et al. (21) reacted several different carbons with carbon dioxide at 1000°C . They found increases in total pore volume and macropore volume with burnoff. Surface area increased with burnoff up to about 10 to 20% burnoff and decreased slightly with higher burnoffs. This they took as evidence of growth of micropores until these grow into one another thereby destroying surface area. They did not present values of micropore volume or distribution. These observations are consistent with those of the present work which indicated micropore growth at low burnoffs and decreasing micropore volumes at higher burnoffs. They also concluded that only a small portion of the surface area participated in the oxidation reaction and that little of this was micropore surface. This is also consistent with the observations on non-uniform surface reactivity in the present work. They made no observations with respect to the opening of closed pores.

Chiche et al. (25) studied the pore structures of two carbonized coals activated with steam at 900°C . They found that surface area from low-angle X-ray scattering was much greater than nitrogen surface area in the starting materials, indicating a large volume of micropores inaccessible to nitrogen. As burnoff proceeded, they found that the X-ray surface area increased little, but the nitrogen surface area increased rapidly, and the two became essentially the same at high burnoff. This indicates that burnoff was opening initially closed pores. Indeed, they concluded that the principle effect of activation was to expose the already existing pore structure. They also found that pore volume increased with burnoff up to 40 to 50% burnoff and that most of the pore-volume increase occurred in the micropores rather than the macropores. Their observations and conclusions are similar to those of the present study, except for the predominance of micropore over macropore volume growth.

Chiche et al. found some differences in behavior between the two coals. They also found that samples that had been ground and briquetted behaved somewhat differently than granular material. The principle difference noted was that in the granular form of the high rank coal, micropore volume steadily decreased with activation. Briquetted samples of this coal, on the other hand, showed micropore growth. They concluded that the optimal pore structure for a starting material for activated carbon would be bimodal, containing micropores to provide surface area and large macropores to provide access to the interior of the particle. They contend that macropores in the radius range .5 to 5μ contribute little to activation in that they burn and consume carbon, but provide little surface area.

Donnett et al. (26) prepared activated carbon from coal by flotation to reduce mineral content, followed by partial oxidation by air at 225-325°C, carbonization at 650°C and then reaction with steam at 900°C. Throughout the carbonization step, they found that surface area and micropore volume measured by carbon dioxide adsorption exceeded those measured by nitrogen adsorption. They also found that oxygen was driven off, and "crater-like" pores in the 10 to 500 Å radius range were formed by carbonization. Higher oxygen contents, from higher temperature air oxidations, resulted in larger crater-like pore and enlarged small micropores. Steam activation to 50% burnoff resulted in both increased surface area and increased micropore volume, and all the surface area became accessible to nitrogen. Activation to 60 to 70% burnoff resulted in little additional change. They did not report macropore volumes. Their results are in several respects similar to those of the present study, but differ in that considerable micropore growth was observed even at high burnoffs.

Singh (58) studied steam activation of an anthracite coal at 830 and 900°C. He concluded that in the 2.5 to 12 Å diameter range, preheating the coal to the reaction temperature created new pores and that activation opened blocked pores (i.e., made smaller pores accessible to larger molecules) and caused the pores to grow larger. Implicit in his results was the fact that pores larger than 12 Å diameter grew in volume more rapidly than those smaller.

Marsh and Rand (61) recently reported on studies of the changes in porous structure of carbon upon gasification. They found that, with a very pure carbon (polyfurfuryl alcohol carbonized at 850°C) reacted with carbon dioxide at 800°C, there was micropore growth by burning and by the opening of closed pores. The closed pores were opened during the first 10% burnoff. The micropore volume per g of starting material increased with burnoff to a maximum at about 60% burnoff, and then decreased. When iron or nickel was added to the carbon, to catalyze the reaction with carbon dioxide, macropores were formed. There was no micropore growth until after the metal had become oxidized and its catalytic activity thereby eliminated. They also observed that carbon monoxide added to the reactant gas enhanced micropore growth in the carbon.

These several studies, plus the present work, have the following results in common: gaseous activation of carbons has as a major effect the opening, or making accessible, of micropore volumes already present in the carbon; pores increase in size due to activation, but growth is not proportional to surface area (the surface is not uniformly reactive to the reactant gas with macropore surface generally appearing to be more reactive); activation increases micropore volume and surface area at low burnoffs, but as burnoff increases, micropore volume and area tend to be relatively constant or even decrease. The most substantial difference between the observations of the

present work and those of other investigators was that in the present study there was essentially no burning in the micropores, while others have found that there apparently was burning in the micropores.

Putting all these results together, several general observations about activation and pore structure can be made. The pore structure of a porous carbon is affected by heating in inert gases. The effect tends to be one of increased total and macropore volumes and decreased micropore volume. The gas is important; greater pore volume changes occur in helium than in nitrogen. The burnoff of material tends to be non-uniform, with far more burnoff per unit area occurring in macropores than in micropores. In some cases there is little or no burning in micropores, while in other cases there appears to be substantial burning in micropores. In any case, the principle effect of activation upon micropores, and thus upon surface area, is to make accessible micropores already present in the starting material. The relatively lower reactivity of micropore surface than macropore surface may be due to diffusion-limited reaction in the micropores, but more probably it is due to a non-uniform distribution of reactive sites. Indeed, there appears to be a non-uniform distribution of reactive sites even within the macropores. The exposure and growth of micropores and surface area occur mainly at low burnoffs (usually less than 20%), and at increased burnoffs, micropore volume and surface area remain relatively constant or even decrease.

It is interesting to examine the results of a recent study on gaseous reactivation of carbons used in wastewater treatment in the light of the present knowledge of the activation process. Juhola and Tepper regenerated spent activated carbon from the Pomona, California tertiary sewage treatment plant (13). They found that once-spent carbon could be regenerated to give essentially the same properties as the virgin carbon, but that carbon spent at least twice and regenerated at least once could then not be regenerated to give the properties of the virgin carbon. In particular, they found that although the mercury and helium densities and the molasses number could be matched with those of the virgin carbon, the iodine number was lower. This indicates that the carbon contained fewer pores in the 5 to 14 Å radius range. They also pointed out that a phase of the reactivation process, which they called baking, involved carbonization of adsorbed organic materials. It was observed in the present study that little or no reaction occurred in the micropores, which include those that are measured by the iodine number but not by the molasses number. Thus, it is proposed that carbonization deposits carbon on pore surfaces and that regeneration removes little, if any, of the deposited carbon from the micropores. Successive use and regeneration of activated carbon would thus result in an accumulation of carbon in the micropores and a progressive decrease in micropore volume and hence in iodine number. This explanation suggests that, unless some way could be found to make the carbon in the micropores more reactive, it should not be expected

that regeneration would recover the micropore volume, and hence iodine number and surface area, of the virgin carbon.

SECTION VII

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SECTION VIII

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SECTION X

GLOSSARY

Terms and Abbreviations:

Activated Carbon - Any form of carbon with large pore volume and surface area capable of adsorbing gases or liquid solutes.

Activation - The process of reacting a carbon, usually with an oxidizing gas, to produce activated carbon.

BET Surface Area - Surface area of a porous solid determined from gas adsorption, usually nitrogen, by the method of Brunauer, Emmett and Teller.

Burnoff - Fraction or percentage of the mass of starting material removed by reacting with oxidizing gas.

Calcinate - Carbon prepared by heating in inert atmosphere to 600 - 800°C.

Carbonization - Devolatilization and cracking of adsorbed hydrocarbons which leaves carbon.

Char - Carbon prepared by heating in inert atmosphere to temperatures up to ca. 500°C.

Chemical rate controlled - Reaction can occur no faster than the inherent chemical reaction rate.

Crystallites - Small crystals of graphitic structure from perhaps 5 to 2000 Å in thickness.

Diffusion controlled or limited - Reaction can occur no faster than a rate determined by the rate of diffusion of reactants or products.

Helium density - Density of solid carbon determined by helium displacement which is the mass of carbon divided by volume not penetrated by helium.

Macropores - Pores with radii greater than 100 Å.

Macropore volume - Volume determined by mercury penetration which includes pores with radii between 100 Å and 51 μ.

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Mercury density - Density of solid carbon determined by mercury displacement at ca. 1.7 psia, or mass of carbon divided by the sum of volume of carbon and volume of pores.

Micropores - Pores with radii less than 100 Å.

Micropore volume - Volume of micropores, determined as total pore volume minus macropore volume.

Pores - Internal voids in a carbon particle.

Porosity - Total pore volume divided by total particle volume (carbon plus pores).

Porous structure - Measurable properties of porous carbon such as pore volumes, volume distribution, and surface area.

Starting Material - Material to be reacted at zero burnoff, but after loss of volatiles at reaction temperature.

STP - Standard temperature and pressure: 0°C, 1 atm.

Total pore volume - Void volume penetrable by helium but not by mercury, or reciprocal of mercury density minus reciprocal of helium density.

USS mesh - United States standard sieve sizes.

Symbols:

A_1 - Preexponential factor in rate coefficients where the subscript number corresponds to that of rate coefficient: A_1 in % C/hr-atm; A_2 in atm⁻¹; A_3 in atm⁻¹.

Å - Angstrom unit, 10⁻¹⁰ meters.

θ - Contact angle of liquid nitrogen in degrees.

dV_1 - Pore volume in an increment of radius, expressed as cc/g.

dS_1 - Surface area in an increment of radius, expressed as m²/g.

ϵ - Porosity, a dimensionless quantity.

ΔE_1 - Activation energy of rate coefficients, expressed as kcal/g mol.

- f - Fraction burnoff, a dimensionless quantity.
- $f(z)$ - Normal probability density function, a dimensionless quantity.
- $F(z)$ - Cumulative normal probability function, a dimensionless quantity.
- i - Subscript which refers to property in an increment of radius.
- k_i - Rate coefficients in equation 3: k_1 in % C/hr atm; k_2 in atm⁻¹; k_3 in atm⁻¹.
- $\ln$ - Natural logarithm, a dimensionless quantity.
- L_i - Length of pores in radius increment.
- m - Meters, or mass of carbon in g.
- μ - Micron, or mean of distribution function.
- o - Subscript which refers to property of starting material.
- p - Pressure in atm or psia, or subscript indicating pore property.
- p_o - Vapor pressure in atm or psia.
- p_{CO} - Partial pressure of carbon monoxide in atm.
- p_{CO_2} - Partial pressure of carbon dioxide in atm.
- r - Pore radius, in either Å or μ .
- r_i - Average radius of a radius increment.
- r_K - Kelvin radius.
- R - Universal gas constant or reaction rate, expressed as %/hr
- ρ_C - Density of solid carbon in g/cc.
- ρ_{He} - Helium density in g/cc.
- ρ_{Hg} - Mercury density in g/cc.
- S - Surface area in m²/g.
- σ - Surface tension in dynes/cm, or standard deviation of distribution.

- t - Thickness of adsorbed film in $\text{\AA}$, or time in hr.
- T - Temperature in $^{\circ}\text{K}$.
- θ - Contact angle of mercury in degrees.
- v - Specific volume of liquid nitrogen in cc/g.
- V - Volume in cc/g.
- $\bar{V}_C$ - Volume of solid carbon, expressed as cc/g of starting material.
- $\bar{V}'_C$ - Volume of solid carbon after burnoff, expressed as cc/g of starting material.
- V_C - Volume of solid carbon in cc/g.
- $\bar{V}_{cp1}$ - Volume of closed pores opened by reaction, expressed as cc/g of starting material.
- $\bar{V}_{cp2}$ - Volume of closed pores not opened by reaction, expressed as cc/g of starting material.
- $\bar{V}_f$ - Volume of pores created only by burning of carbon, expressed as cc/g of starting material.
- $\bar{V}_o$ - Constant in normalized pore volume, expressed as cc/g of starting material.
- V_p - Total pore volume in cc/g.
- $\bar{V}_p$ - Total pore volume in cc/g of starting material.
- $\bar{V}_{pm}$ - Micropore volume in cc/g of starting material.
- $\bar{V}_{pM}$ - Macropore volume in cc/g of starting material.
- $\bar{V}_T$ - Constant in normalized pore volume, expressed as cc/g of starting material.
- x - Dummy variable in distribution function.
- z - Any random variable of a normal distribution.

SECTION XI

APPENDICES

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APPENDIX 1: Model of Pore-Volume Change

A method is developed herein for computing the expected change in total, macropore, and micropore volumes.

It is assumed that the total volume of a carbon particle (that is, the volume of carbon plus the volume of pores as determined by mercury density) does not change with burnoff. Or equivalently, that all mass removed by burning is removed from the interior surface. The mercury density of the starting material is thus given by

$$\rho_{\text{Hgo}} = \frac{m}{V_C + V_p} \quad (1-1)$$

The mercury density of the material after burnoff is given by

$$\rho_{\text{Hg}} = \frac{(1-f)m}{V_C + V_p} \quad (1-2)$$

Dividing equation 1-2 by 1-1 gives

$$\rho_{\text{Hg}} / \rho_{\text{Hgo}} = 1 - f \quad (1-3)$$

The total measurable volume of a sample, in cc/g of starting material, will be that of the starting material plus the change in pore volume;

$$\bar{V}_p = \bar{V}_{p0} + \Delta \bar{V}_p \quad (1-4)$$

The initial pore volume is given by

$$\bar{V}_{p0} = \frac{1}{\rho_{\text{Hgo}}} - \frac{1}{\rho_{\text{Heo}}} \quad (1-5)$$

$\Delta \bar{V}_p$ is the change in the total pore volume due to activation and can be expressed as follows:

$$\Delta \bar{V}_p = \frac{1}{\rho_{\text{Heo}}} - \frac{1-f}{\rho_{\text{He}}} \quad (1-6)$$

The first term, $1/\rho_{\text{Heo}}$, is the volume per unit weight of all material impenetrable by helium in the starting material, and $(1-f)/\rho_{\text{He}}$ is the volume impenetrable by helium in a sample in cc/g of starting material. The

difference between these two quantities gives the change in the volume impenetrable by helium. If the particle size has not changed, this quantity will be the change in interior pore volume. It is to be emphasized that this method includes the assumption that the particle volume does not change by activation.

Combining equations 1-4, 1-5 and 1-6 results in

$$\bar{V}_P = \frac{1}{\rho_{Hgo}} - \frac{1-f}{\rho_{He}} \quad (1-7)$$

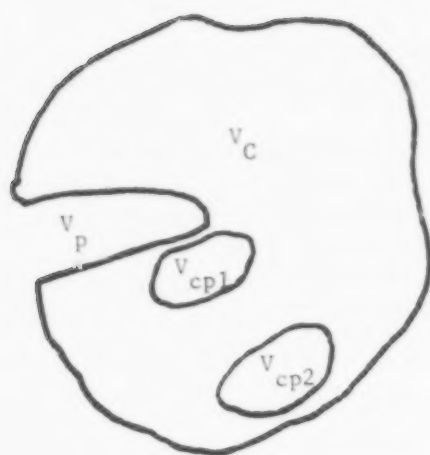
$\bar{V}_P$ determined in this manner is referred to as the "calculated-by-model" total pore volume in cc/g of starting material.

It is to be noted that this calculated pore volume makes use of experimental data. However, it is used to calculate the expected pore volume from the mercury density of the starting material and from the helium density of the sample, and it assumes a constant particle volume. Hence, since it uses a property of the starting material, an assumption about the particle size and only one measured property of a sample, it is more predictive than the measured pore volume as given by equation 1-5.

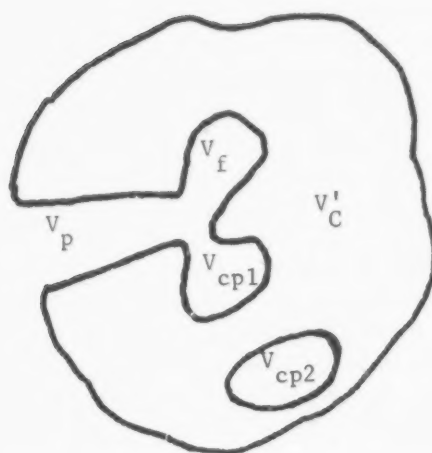
Micropores are considered to be all pores less than $.01\mu$ in radius. The micropore volume has been obtained by subtracting the measured macropore volume from the measured total pore volume.

It was noted in the experimental results that the micropore-volume curves have a similar shape to those of helium densities, suggesting a relationship between the two. As was pointed out earlier, the change in helium density is considered to be due to the opening of closed pores. This suggests that changes in micropore volume may be due to the opening of closed pores. To examine this possibility, a model will be developed for predicting micropore volumes as a result of opening closed pores. Results predicted by the model will then be compared with the actual experimental results.

Figure 18, a and b, will be used to illustrate the changes occurring. Figure 18a represents a particle of the starting material, and Figure 18b represents the same average particle after activation. A basis of one g of starting material will be taken. After burning, the weight of the same particles will be $(1-f)$ g, and the weight of each particle will be assumed to be in that same ratio to its initial weight.



(a)



(b)

FIGURE 18. SCHEMATIC DIAGRAM OF CARBON PARTICLE

The mercury and helium densities can be expressed as follows:
starting material,

$$\rho_{\text{Hgo}} = \frac{\text{weight of carbon, g}}{\text{Total volume of particle, cc}} = \frac{1}{\bar{V}_C + \bar{V}_p + \bar{V}_{\text{cp1}} + \bar{V}_{\text{cp2}}} \quad (1-8)$$

$$\begin{aligned} \rho_{\text{Heo}} &= \frac{\text{weight of carbon, g}}{\text{vol. of solid carbon + any closed pores, both in cc}} \\ &= \frac{1}{\bar{V}_C + \bar{V}_{\text{cp1}} + \bar{V}_{\text{cp2}}} \end{aligned} \quad (1-9)$$

sample after reaction,

$$\begin{aligned} \rho_{\text{Hg}} &= \frac{\text{weight of carbon remaining, g}}{\text{total volume of particles, cc}} \\ &= \frac{1-f}{\bar{V}'_C + \bar{V}'_f + \bar{V}'_p + \bar{V}_{\text{cp1}} + \bar{V}_{\text{cp2}}} \end{aligned} \quad (1-10)$$

$$\begin{aligned} \rho_{\text{He}} &= \frac{\text{weight of carbon remaining, g}}{\text{volume of carbon remaining + any closed pores, both in cc}} \\ &= \frac{1-f}{\bar{V}'_C + \bar{V}_{\text{cp2}}} \end{aligned} \quad (1-11)$$

Assuming that there is no significant change in the volume of the particle due to carbon burnoff, $\bar{V}'_f$ can be determined by dividing the fraction burned off by the solid-carbon density. In these calculations, the density of solid carbon was assumed to be 2.0 g/cc.

To calculate the volume change due to opening of closed pores, the following steps will be taken:

subtract 1-11 from 1-9 to give,

$$\frac{1}{\rho_{\text{Heo}}} - \frac{1-f}{\rho_{\text{He}}} = \bar{V}_C - \bar{V}'_C + \bar{V}_{\text{cp1}} = \bar{V}'_f + \bar{V}_{\text{cp1}} \quad (1-12)$$

This expression is the pore-volume change due to both burn-off and opening of closed pores. Therefore, from 1-12,

$$\bar{V}_{cpl} = \frac{1}{\rho_{Heo}} - \frac{1-f}{\rho_{He}} - \bar{V}_f \quad (1-13)$$

The carbon and hence the pore-volume change due to burnoff is,

$$\bar{V}_f = \frac{f}{\rho_C} = \frac{f}{2.0} \quad (1-14)$$

Thus, the volume of closed pores opened as a result of burning is given by,

$$\bar{V}_{cpl} = \frac{1}{\rho_{Heo}} - \frac{1-f}{\rho_{He}} - \frac{f}{2.0} \quad (1-15)$$

Assuming that all the closed pores opened up are micropores and that no burning occurs in the micropores, the change in volume of micropores (in cc/g of starting material) will be given by equation 1-15, and the volume of micropores will be given by ,

$$\bar{V}_{pm} = \bar{V}_{pmo} + \bar{V}_{cpl} = \bar{V}_{pmo} + \frac{1}{\rho_{Heo}} - \frac{1-f}{\rho_{He}} - \frac{f}{2.0} \quad (1-16)$$

If all the burning occurs in the macropores and the macropore-volume change is due only to burning, the macropore-volume change will be given by equation 1-14, and the macropore volume (in cc/g of starting material) will be given by ,

$$\bar{V}_{pM} = \bar{V}_{pMo} + \frac{f}{2.0} \quad (1-17)$$

If the macropore-volume change is due to opening of closed pores as well as to burning, the total change in pore volume, given by equation 1-6, must be added to the initial macropore volume to give,

$$\bar{V}_{pM} = \bar{V}_{pMo} + \frac{1}{\rho_{Heo}} - \frac{1-f}{\rho_{He}} \quad (1-18)$$

It is interesting to note that if the change in micropore volume (given by 1-15) and the change in macropore volume (given by 1-14) are added to the initial total pore volume (given by 1-5), the result is 1-7 which is the expression for total pore volume developed above. Thus, the equations are consistent.

APPENDIX 2: Macropore Burning Model

Two different mathematical models are developed to describe the change in the cumulative macropore volume due to burning. The first, model 1, is based on the assumption of uniform reaction rate per unit surface area throughout the macropores. The second, model 2, is based on assuming that the reaction rate in a pore-size increment is proportional to the initial pore volume present in that increment.

Model 1

For cylindrical pores of average radius r_i and length L_i , in a radius increment $d \ln r$, the volume dV_i and the surface area dS_i are given by ,

$$dV_i = \pi r_i^2 L_i \quad (2-1)$$

$$dS_i = 2\pi r_i L_i \quad (2-2)$$

Dividing 2-2 by 2-1,

$$dS_i = \frac{2 dV_i}{r_i} \quad (2-3)$$

A normalized, pore-volume, distribution function is defined by,

$$f(z) = \frac{d(\bar{V}_i - \bar{V}_o) / (\bar{V}_T - \bar{V}_o)}{d \ln r} \quad (2-4)$$

Hence,

$$dV_i = (\bar{V}_T - \bar{V}_o) f(z) d \ln r \quad (2-5)$$

Substituting 2-5 into 2-3 gives for the surface area in the increment,

$$dS_i = \frac{2 dV_i}{r_i} = \frac{2}{r_i} (\bar{V}_T - \bar{V}_o) f(z) d \ln r \quad (2-6)$$

If m_o is the initial weight of carbon and m is the weight of carbon left after time t , then the rate of reaction, R , is given by ,

$$R = - \frac{d(m/m_o)}{dt} = - \frac{dm}{m_o dt} \quad (2-7)$$

The change in carbon mass, dm , is $\rho_C dV_C$ which is the carbon density times the change in volume of carbon. The change in carbon volume is $-dV_p$, the negative of the change in pore volume. Substituting this into 2-7 and dividing both sides by the total initial surface area, S_o , gives,

$$\frac{R}{S_o} = \frac{\rho_C dV_p}{S_o m_o dt} \quad (2-8)$$

Now, assuming that the reaction rate per unit surface area is a constant, the reaction rate in pores of average radius r_i is given by,

$$R_i = \frac{R}{S_o} dS_i \quad (2-9)$$

and substituting for dS_i from 2-6 yields,

$$R_i = \frac{R}{S_o r_i} (2(\bar{V}_T - \bar{V}_o) f(z) d \ln r) \quad (2-10)$$

From 2-8 the rate in the pores is also given by,

$$R_i = \frac{\rho_C d(d\bar{V}_i)}{dt} \quad (2-11)$$

Equating 2-10 and 2-11, rearranging and integrating gives

$$\int_{d\bar{V}_{i0}}^{d\bar{V}_i} d(d\bar{V}_i) = \frac{2}{\rho_C S_o r_i} ((\bar{V}_T - \bar{V}_o) f(z) d \ln r) \int_0^t R dt \quad (2-12)$$

Integrating equation 2-7 gives,

$$\int_0^t R dt = - \int_{m_0}^m \frac{dm}{m_0} = \frac{m_0 - m}{m_0} = f \quad (2-13)$$

Thus, from 2-12, the change in volume of pores of initial average radius r_i is given by,

$$\Delta(d\bar{V}_i) = \frac{f(2(\bar{V}_T - \bar{V}_0)f(z) d \ln r)}{\rho_C S_0 r_i} \quad (2-14)$$

As burning occurs on the pore surface, the radius will also change. If r_i is the mean pore radius in an increment at time zero and r is the mean radius at time t , the change in volume of the pores is given in terms of radius by,

$$\pi L_i (r^2 - r_i^2) = \frac{(dS_i)f}{S_0 \rho_C} = \frac{2\pi r_i L_i f}{S_0 \rho_C} \quad (2-15)$$

Solving for r ,

$$r = \sqrt{r_i^2 + \frac{2r_i f}{S_0 \rho_C}} \quad (2-16)$$

Using equations 2-14 and 2-16, the new volume and radius corresponding to any increment of the volume distribution of the starting material could be calculated as a function of burnoff. A computer program was written to do the calculations. A volume distribution function for the starting material is needed. This could be in numerical form, as the actual raw cumulative pore-volume data, or in functional form as described in Appendix 3.

Model 2

Assuming that the pore-volume change is directly proportional to the initial pore volume in an increment, equations are derived to predict the pore-volume distribution for a sample of a given burnoff. It is to be noted that this assumption is not made on theoretical grounds, rather as an empirical observation.

The total macropore-volume change due to burning is given by equation 1-13. The change in volume in any increment, $\Delta d\bar{V}_i$, is proportional to $d\bar{V}_i$ and is equal to the total change in pore volume times the fraction of the total pore volume in the increment, thus,

$$\Delta d\bar{V}_i = \frac{f d\bar{V}_i}{\rho_C (\bar{V}_T - \bar{V}_o)} \quad (2-17)$$

The change in volume in terms of radius is expressed by the left-hand side of 2-15; equating this to 2-17, substituting for $d\bar{V}_i$ from 2-1, and solving for r gives,

$$r = r_i \sqrt{1 + \frac{f}{\rho_C (\bar{V}_T - \bar{V}_o)}} \quad (2-18)$$

Equations 2-17 and 2-18 were used to calculate the new pore volume and average radius of points on the starting material volume-distribution curve for various burnoffs. A computer program was written to do the calculations.

APPENDIX 3: Fitting Macropore Distributions

As was noted in the Results section, the macropore-distribution curves were found to resemble the log-normal density function. The log-normal density function is given by the expression (59) ,

$$f(z) = \frac{1}{\sqrt{2\pi}} \exp \left(-\frac{1}{2} \left((\ln x - \mu)/\sigma \right)^2 \right) \quad (3-1)$$

and the cumulative value is given by (59) ,

$$F(z) = \int_{-\infty}^z \frac{1}{\sqrt{2\pi} \sigma} \exp \left(-\frac{1}{2} \left((\ln x - \mu)/\sigma \right)^2 \right) d \ln x \quad (3-2)$$

Values of $F(z)$, the standard cumulative normal distribution, are tabulated (59) or may be calculated by common computer subroutines. In the present work, $F(z)$ corresponds to the normalized cumulative macropore volume, $(\bar{V}_{pM} - \bar{V}_o)/(\bar{V}_T - \bar{V}_o)$. The density function, $f(z)$, corresponds to the normalized volume-distribution function, $(d(\bar{V}_{pM} - \bar{V}_o)/(\bar{V}_T - \bar{V}_o))/d \ln r$. In equations 3-1 and 3-2, x corresponds to r , and μ and σ are the mean and standard deviation of the distribution function. Thus,

$$\begin{aligned} f(z) &= \frac{1}{\sqrt{2\pi}} \exp \left(-\frac{1}{2} \left((\ln r - \mu)/\sigma \right)^2 \right) \\ &= (d(\bar{V}_{pM} - \bar{V}_o)/(\bar{V}_T - \bar{V}_o))/d \ln r \end{aligned} \quad (3-3)$$

and,

$$\begin{aligned} F(z) &= \int_{-\infty}^{\ln r} \frac{1}{\sqrt{2\pi} \sigma} \exp \left(-\frac{1}{2} \left((\ln r - \mu)/\sigma \right)^2 \right) d \ln r \\ &= (\bar{V}_{pM} - \bar{V}_o)/(\bar{V}_T - \bar{V}_o) \end{aligned} \quad (3-4)$$

A non-linear least-squares fitting program was used to take mercury-porismeter data in the form of cumulative volume at various pore radii and to obtain from that the best values of the constants μ , σ , $\bar{V}_T$, and $\bar{V}_0$ (44, 45, 60). With these values, equation 3-3 could be used to calculate the normalized volume-distribution curve, and equation 3-4 could be used to calculate the normalized cumulative-volume curve. The calculated cumulative-volume curves fit the data with an average absolute error of 2% (60).

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*Adsorbents, Carbon Activation, Porous Structure

27 Abstract
Reaction rates and porous structures of a calcined Wyoming coal activated by air and by carbon dioxide and a graphite activated by carbon dioxide were measured. Total, macropore and micropore volumes, surface area and pore-size distributions were determined as functions of burnoff.

In 1-mm-diameter calcined coal particles, the overall reaction rate was chemical rate limited at temperatures as high as 961°C and rates as high as 106%/hr. In 19-mm-diameter graphite cylinders, the rate at 1030°C was diffusion limited. In graphite, pore growth by end-burning of crystallites was an important mechanism. In calcined coal, pore-volume changes occurred due to heating, carbon burnoff and the opening of closed pores present in the starting material. Burnoff of carbon occurred essentially entirely in macropores. Up to 12% burnoff, the closed pores that were opened were micropores; above 12% burnoff they were macropores.

In order to develop large micropore volumes and hence large surface areas by gas activation, a micropore structure must be present in the starting material.

The report includes 13 tables, 18 figures and 61 references. (West-Colorado)

Abstractor	Institution
Ronald E. West	Colorado University

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